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FLUORINE SYSTEMS HANDBOOK, SECTION VI, DYNAMIC COMPATIBILITY OF FLUORINE WITH METALS

Roger E. Anderson

Aerojet Liquid Rocket Company

Prepared for:

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FLUORINE SYSTEMS HANDBOOK

SECTION VI

DYNAMIC COMPATIBILITY OF FLUORINE WITH METALS

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Technical Report AFRPL-TR-72-119
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Air Force Rocket Propulsion Laboratory
Director of Science and Technology
Air Force Systems Command
United States Air Force
Edwards Air Force Base, California

FOREWORD

This special technical report is submitted in compliance with and partial fulfillment of the requirement of Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants," Phase III - Data Publication, Task 4 - Special Technical Reports (B005). The effort under this contract was sponsored by the Air Force Rocket Propulsion Laboratory under Air Force Project 5730 Task 07. The Air Force Project Engineer was Capt Howard M. White.

This program was conducted by the Chemical Processes and Materials Section of Aerojet Liquid Rocket Company with Dr. S. D. Rosenberg serving as Program Manager and Dr. E. M. Vander Wall serving as Project Chemist.

The work reported in this document was performed from 3 January to 31 August 1972.

The following technical personnel contributed to the compilation and analysis of the data and information contained in this report: R. E. Anderson, R. L. Beegle, Jr., and J. A. Cabeal.

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This report has been reviewed and is approved.

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13 ABSTRACT

This document is a special technical report prepared under Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants" and is issued as Section VI of the Fluorine Systems Handbook (NASA CR-72064, Douglas Aircraft Co., Inc., Missiles and Space Div., Santa Monica, California, Contract NASw-1351, 1 July 1967). It is a compilation of all pertinent data and design criteria concerning the dynamic compatibility of fluorine with metals. The information was obtained in the course of the contract which involved both literature search and review and original experimental investigations.

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SECTION I

INTRODUCTION

The use of fluorine, F_2, in military systems has attracted considerable attention over a period of years. As a result, a rather large number of basic research, component, and technology programs involving this very reactive oxidizer has been conducted. The inherent reactivity of fluorine is well known and, as a consequence, materials compatibility problems have always figured prominently in such programs. A significant amount of compatibility data has been generated, compiled, and factored into successive programs. In most cases, the application of available compatibility data (and proper cleaning, passivation, and handling procedures) has permitted the use of fluorine in static systems without incident. Unfortunately, practically all real systems employing fluorine are dynamic, while most compatibility data have been established for static conditions. Many incidents, ranging from benign to catastrophic, have occurred. Almost invariably, the origin of an "incident" can be traced to a dynamic fluorine/material interface and has been attributed to some poorly defined, basic dynamic incompatibility problem or to "contamination". Post-incident inspections often cannot discriminate between these two possibilities.

The compatibility data available on fluorine up to 1965 and/or 1967 were compiled in Design Handbook for Liquid Fluorine Ground Handling Equipment*, Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems**, and Fluorine Systems Handbook***. Although these documents are excellent data sources on the compatibility of fluorine with many materials, the data relating to the dynamic compatibility of fluorine with metals were scant. That inadequacy in data and recurring problems in systems employing fluorine, which were in many cases attributed to an inadequate understanding of dynamic compatibility, prompted the Air Force Rocket Propulsion Laboratory to issue Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants," to Aerojet Liquid Rocket Company. The objective of this program was to establish design criteria on the dynamic compatibility of liquid and gaseous fluorine and chlorine pentafluoride with metallic materials. The program covered both

*Design Handbook for Liquid Fluorine Ground Handling Equipment, 2nd ed., AFRPL-TR-65-133, Aerojet-General Corp., Sacramento, California, Contract AF 04(611)-10541, August 1965.

**Schmidt, H. W., Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems, NASA SP-3037, (Lewis Research Center, Cleveland, Ohio), NASA, Washington, D.C., 1967.

***Fluorine Systems Handbook, NASA CR-72064, Douglas Aircraft Co., Inc., Missiles and Space Div., Santa Monica, California, Contract NASw-1351, 1 July 1967.

I, Introduction (cont.)

literature search and review and experimental evaluation of the effects of gas velocity, adiabatic compression, liquid impact, flexing/film degradation, vibration/film degradation, and liquid phase shock wave ("water hammer") on oxidizer/metal reactions.

This document is a special technical report prepared under Contract F04611-72-C-0031 and is issued as Section VI to the Fluorine Systems Handbook, NASA CR-72064. It is a compilation of all the pertinent data and design criteria which have been obtained in the course of the contract from both the literature search and review and experimental portions of the program.

Users of fluorine and designers of systems employing fluorine are cautioned that although the information contained herein clearly indicate that the metals investigated can withstand significant inputs of energy from various dynamic system effects without dangerous consequences, these levels of compatibility have been obtained under laboratory conditions where test equipment and metal specimens have been scrupulously cleaned and exposed to fluorine of high quality. Failures to follow recommended cleaning and passivation procedures (see Appendices III-4 and III-5 of the Fluorine Systems Handbook) can lead to major failure in spite of the use of the most compatible materials. The information in this section strongly suggests that most instances of burnthrough, explosions, etc., in dynamic systems involving the metals covered here are the result of contaminants that may be undetectable in the relatively complex dynamic systems or are released to the fluorine environment by the action of the fluorine on the system.

SECTION II

METALS BEHAVIOR IN HIGH TEMPERATURE GASEOUS FLUORINE FLOW SYSTEMS

A. EFFECT OF TEMPERATURE AND VELOCITY ON F_2/METAL SYSTEMS

Under Contract F04611-72-C-0031, Dynamic Compatibility of Halogen Propellants, (Reference 1), the Aerojet Liquid Rocket Company conducted flow tests with gaseous, preheated F_2 on heated specimens of nine metals. The metals investigated were:

304-L Stainless Steel	6061-T6 Aluminum
347 Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
	Nickel 200

The flow specimens consisted of drilled passages 0.020-in. dia by 0.250-in. long in the test materials. The specimens were carefully cleaned (but not passivated) and rigidly mounted in a Nickel 200 tube which was electrically heated. The system was orificed upstream and/or downstream to provide desired flowrates, velocities, and pressure drops through the test specimens. Instrumentation included specimen temperature at a point 0.010-in. from the flow passage, specimen pressure drop, upstream gas temperature, and outside tube wall temperature. In test operation, the system was orificed to produce one of three basic flow conditions in the specimen: (1) static, (2) subsonic flow, or (3) sonic flow. The incoming F_2 and the specimen were then simultaneously electrically heated to produce a nominal temperature rise rate of 10°F/sec. Plots of temperature versus time were used to define both minor and major exotherms and plots of specimen pressure drop versus time or temperature for specimens flowing in the subsonic regime were used to define major changes in film buildup or degradation. In most tests which were initially flowing in a subsonic regime, film buildup during the course of a test was sufficient to cause the flow passage to become sonic prior to a major exotherm or change in geometry. Thus, terminal material effects in the subsonic flow regime could not normally be ascertained. The F_2 gas pressure upstream of the test specimen was nominally 100 psia.

The results of these tests are summarized in Table I wherein threshold temperatures and the corresponding material responses are defined for the various materials and flow regimes. Although some of the materials tested under some of the flow conditions exhibited very little or very gradual geometric and/or thermal responses as temperature increased up to the point a very dramatic change occurred, the most common behavior was for the materials to undergo several "minor or nonfailing" responses prior to a "major or failing-type" response. This latter common behavior makes the definition of a single threshold set of dynamic conditions for incipient failure difficult because a

TABLE I

RESPONSE OF METALS TO GASEOUS FLUORINE AT VARIOUS TEMPERATURES AND FLOW STATES

Material	Static		Subsonic Flow		Sonic Flow	
	Threshold Temp., °F	Material Response	Threshold Temp., °F	Material Response	Threshold Temp., °F	Material Response
6061-T6 Al					~1000	Probable onset of film buildup.
					1150	Major exotherm and loss of specimen.
OFHC Cu	1090*	Probable onset of film buildup.	1000 σ = 40*	Onset of film buildup.	855	Onset of a series of small exotherms and endotherms.
	1230*	Apparent exothermic reaction (slight).	1190 σ = 25*	Significant change in film buildup/thermal effects.	1150	Significant exotherm.
	1400*	Apparent endothermal reaction (slight).	1380 σ = 25*	Moderate exotherms and film changes.	1250	Relative large exotherm.
	1585*	Significant exotherm, modest specimen attack.	1525 ± 58*	Major exotherm and loss of specimen material.	1485	Major exotherm reaching a max. temp. of ~2100°F, specimen suffers modest attack.
321 S.S.	1145	Probable onset of rapid film buildup.			1115	Probable onset of rapid film buildup.
	1890	Onset of a series of exotherms reaching a max. temp. of 2475°F, significant material loss.			1700	Major exotherm with significant loss of specimen material.
304-L S.S.	1285	Probable onset of rapid film buildup.			1140	Probable onset of rapid film buildup.
	1930	Major exotherm with significant loss of specimen material.			1722	Major exotherm with significant loss of specimen material.
347 S.S.			1335	Onset of rapid film buildup.	1315	Probable onset of rapid film buildup.
	1833	Major exotherm with significant loss of specimen material.			1723 σ=2	Major exotherm with significant loss of specimen material.
A-286 S.S.	~1400	Probable onset of rapid film buildup.	1350	Onset of rapid film buildup.	1350	Probable onset of rapid film buildup.
	1900	Onset of a series of exotherms reaching a max. temp. of 2320°F, significant material loss.			1704	Major exotherm with significant loss of specimen material.
Inconel 718			~1675	Onset of very rapid film buildup.	1675	Onset of a series of exotherms reaching a max. temp. of 2480°F, flow passage corroded closed.
Monel K-500	1695	Significant exotherm.	1575	Onset of very rapid film buildup.	1520	Probable onset of rapid film buildup.
	1905	Major exotherm reaching max. temp. of ~2400°F, flow passage corroded closed.			1715	Major exotherm reaching max. temp. of 2300°F, flow passage corroded and restricted.
Nickel 200			1785	Onset of a series of exotherms with max. temp. ≥ 2340°F, no significant change in flow passage.	1755	Onset of a series of exotherms with max. temp. >2360°F, no significant change in flow passage.
			≤2300**	No evidence of melting or ignition.		

* Temperature based on outside wall temperature.
**Information based on Reference 2.

II, A, Effect of Temperature and Velocity on F_2/Metal Systems (cont.)

particular "minor or major" material response in terms of these tests could be accentuated or damped in a related but different flow systems. Inspite of this limitation, the data do provide the firmest set of low and high probability threshold temperature and velocity conditions available for a variety of metals subjected to gaseous F_2 in a variety of flow conditions.

On the basis of the test results presented in Table I, the low and high probability threshold temperatures for the various flow conditions, i.e., static, subsonic, and sonic velocity, are presented in Table II and recommended for the guidance of designers. In the use of Table II, it must be recognized that the high probability threshold should never be used for design purposes without specific independent test verification. Additionally, an analysis of test to test variations in repetitive samples shows standard deviations as high as 40°F, suggesting that the low probability thresholds should be reduced approximately 3σ or 120°F when considering limiting design capabilities.

In a related series of fluorine flow tests reported by Duckering (Reference 2), a 0.050-in. wall Nickel 200 tube was electrically heated to selected temperatures and then exposed to gaseous fluorine at ∿260 psig and a velocity of ∿30 ft/sec for 1-sec periods of time. The tests were conducted at specimen temperatures of 1000 to 2000°F at 200°F increments and from 2000 to 2300°F at 100°F increments. There was no evidence of tube melting or ignition in any of the tests. A sonic orifice located downstream of the tube specimen and exposed to gaseous fluorine at ∿140 psia, 200-250°F, and ∿1000 ft/sec was similarly unaffected.

Goodwin and Lorenzo (Reference 3) determined the ignition temperatures of several metals in essentially static gaseous fluorine using two experimental techniques both of which involved electrical heating of metal wire specimens. Temperatures were calculated from current, voltage, and temperature-resistivity data. In "Technique A" an evacuated bomb was filled with gaseous fluorine at atmospheric pressure and the temperature of the specimen was gradually increased until burnout was achieved. In "Technique B" the test specimen was brought to a predetermined temperature in the evacuated bomb before the introduction of fluorine. Fluorine was admitted and the time for the reaction to go to completion was measured. The data obtained from these tests are summarized in Table III. The ignition temperatures defined by the two techniques are in reasonable agreement; however, both techniques give ignition temperatures of questionable accuracy because the effect of preignition reactions on the current, voltage, temperature-resistivity data used in calculating temperatures are not taken into account. The preignition reaction effect appears less significant in "Technique B" and, therefore, probably yields the more reliable data.

TABLE II

LOW AND HIGH PROBABILITY FAILURE THRESHOLD TEMPERATURES FOR THE FAILURE OF METALS IN GASEOUS FLUORINE

Material	Threshold Temperature for a Low Probability of Failure, °F[1]			Threshold Temperature for a High Probability of Failure, °F[2]		
	Static F_2	Subsonic F_2	Sonic F_2	Static F_2	Subsonic F_2	Sonic F_2
6061-T6 Aluminum			1000			1150
OFHC Copper	∿1090	∿1000	855	1585	1525	1485
321 Stainless Steel	1145		1115	1890		1700
304-L Stainless Steel	1285		1140	1930		1720
347 Stainless Steel		1335	1315	1830		1720
A-286 Stainless Steel	∿1400	1350	1350	1900		1700
Inconel 718		∿1675	∿1675			>1675[3]
Monel K-500	∿1695	1575	1520	1905		1715[3]
Nickel 200		∿1785	∿1755			>1755[3]

(1) Temperature at which the onset of a discernible but relatively minor material response is observed in a period of a few seconds. These values, when reduced by ∿120°F to account for test-to-test variations, may be used when considering reasonable limiting design capabilities (excluding stress).

(2) Temperature at which the onset of a major material response is observed in a period of a few seconds or less.

(3) These temperatures correspond to the onset of significant to major exotherms which may be accompanied by the buildup of appreciable quantities of corrosion products. Metal ignition is not evident, however.

TABLE III

IGNITION TEMPERATURES OF METALS IN STATIC GASEOUS FLUORINE

Technique A

Material	Average Ignition Temp., °F	Observed Range of Ignition Temp., °F	Standard Deviation, °F
Molybdenum	398	370 - 428	22
Tungsten	540	500 - 630	45
Monel	745	658 - 819	61
Iron	1241	1233 - 1251	9
302 Stainless Steel	1259	1058 - 1465	164
Copper	1277	1193 - 1377	64
Nickel	2123	1983 - 2226	86
Aluminum	>M.P.		

Technique B

Iron	1144 - 1191
Copper	1272 - 1294
Nickel	2287 - 2311

II, A, Effect of Temperature and Velocity on F_2/Metal Systems (cont.)

Inspection of the data presented in Tables I, II, and III for aluminum, shows: (1) the earliest signs of attack have been observed to occur near 1000°F under sonic flow conditions, (2) a major exotherm occurs at ∿1150°F with sonic fluorine and results in a melting- and/or burnout-type failure, and (3) ignition in static fluorine occurs at or above the melting point of aluminum. A similar inspection of the data on copper shows: (1) the earliest signs of copper attack occur in the temperature range of ∿850 to 1100°F, varying within this range more or less inversely with flow velocity, (2) a number of more significant velocity dependent exotherms, endotherms, and film changes are observed in the temperature range of ∿1150 to 1400°F which may result in ignition under certain poorly defined conditions that are not strongly dependent on velocity, and (3) a major reaction is almost certain to occur when the temperature reaches 1485 to 1585°F. The combined data from References 1 and 3 on austenitic stainless steels indicate: (1) significant attack occurs within the temperature range of ∿1100 to 1400°F, varying within this range somewhat inversely with velocity and the particular stainless steel, (2) ignition may occur within this same temperature range under certain poorly defined conditions apparently not related strongly to flow velocity, and (3) a major reaction involving a large heat release and material loss is almost certain to occur upon reaching a temperature of ∿1700°F under sonic conditions and 1830 to 1930°F under static conditions.

The data on Inconel 718 are difficult to interpret but indicate an important threshold temperature near 1675°F that is quite velocity independent. Gradual film buildup appears to be the significant reaction at temperatures up to this threshold at which point the reaction rate increases rapidly. In some cases this condition appears to cause the film to immediately fail and reform resulting in significant exotherms and formation of corrosion products while in other cases, the film is not disrupted until temperatures of up to 1835°F are reached. Although appreciable quantities of corrosion products and pulse temperatures of over 2400°F have been observed following film failures on Inconel 718, true ignition with the loss of substantial base metal has not been observed.

Monel K-500 undergoes a rapid increase in the rate of film buildup in the temperature range of ∿1500 to 1600°F, apparently varying somewhat inversely with velocity. At a temperature near 1700°F the film may fail in either static or sonic fluorine and result in an exotherm as it reforms. This film may remain intact, however, up to temperatures as high as 1850°F and ∿1900°F in sonic and static fluorine, respectively. Although pulse temperatures approaching 2400°F were recorded following film failures, an appreciable loss of base material was observed in only one case, and true ignition was never observed. An ignition temperature of ∿745°F for Monel as reported in Reference 3, cannot be reconciled with the data from Reference 1.

II, A, Effect of Temperature and Velocity on F_2/Metal Reactions (cont.)

Inspection of the data on nickel from Reference 1 shows the earliest signs of reaction with fluorine occur at ∿1750 to 1800°F and are apparently only slightly influenced by velocity. This onset of reaction appears normally as a series of mildly exothermic film-forming reactions. As temperature increases beyond ∿1900°F, the exotherms may become quite large, increasing the specimen film temperature several hundred degrees (°F) in less than a second. In Reference 1, peak temperatures of greater than 2360°F were recorded while the specimens underwent no significant damage other than the formation of a film. This agrees well with the data of Reference 2 wherein temperatures up to 2300°F in low velocity fluorine caused no evidence of melting or ignition. In Reference 3, the "ignition temperature" of nickel in static fluorine is indicated to be in the range of ∿1980 to 2310°F; however, the indirect method of defining temperature decreases the reliability of the data.

From all the data available, it must be concluded that nickel is the best metal known for containing hot, flowing, gaseous fluorine. In descending order of preference the other metals studied are ranked as follows: Inconel 718 and Monel K-500, austenitic stainless steels, copper, and aluminum.

B. DYNAMIC CORROSION RATES OF REFRACTORY METALS IN FLOWING HIGH TEMPERATURE FLUORINE-ARGON GAS MIXTURES

IIT Research Institute (References 4, 5, and 6) has conducted an extensive investigation of the dynamic corrosion rates of various refractory metals in flowing, high-temperature, fluorine-argon gas mixtures. The test facility was capable of producing variable gas flow conditions and maintaining specimens at temperatures up to 5800°F. A schematic diagram of the test chamber is shown in Figure 1.

Test samples 0.5 x 0.5 x 0.125-in. thick are heated by self-inductance in a thick-walled stainless steel chamber using a 2.5 or 5 Kw induction unit. Thus, the maximum temperature limit is defined by the material under test and the input power. Temperature measurements are made optically through a top sight glass which permits visual observation of specimen deterioration during exposure. Argon and the corrosive gases are metered in precision flow meters and premixed before entering the nozzle assembly. Fluorine is passed through a sodium bifluoride trap to remove residual hydrogen fluoride prior to entering the fluorine flow meter. The nozzle assembly consists of thick-walled stainless tubing swaged to obtain a 0.036-in. exit nozzle. During testing, the nozzle exit is maintained at a fixed distance (usually 1 in.) from the test specimen. Test specimens are supported in the induction coil by a 0.125-in. tungsten rod, which is split to minimize the contact area and to stabilize the test specimen. Exiting reaction products are passed through an activated charcoal absorption column prior to exhausting through a laboratory hood.

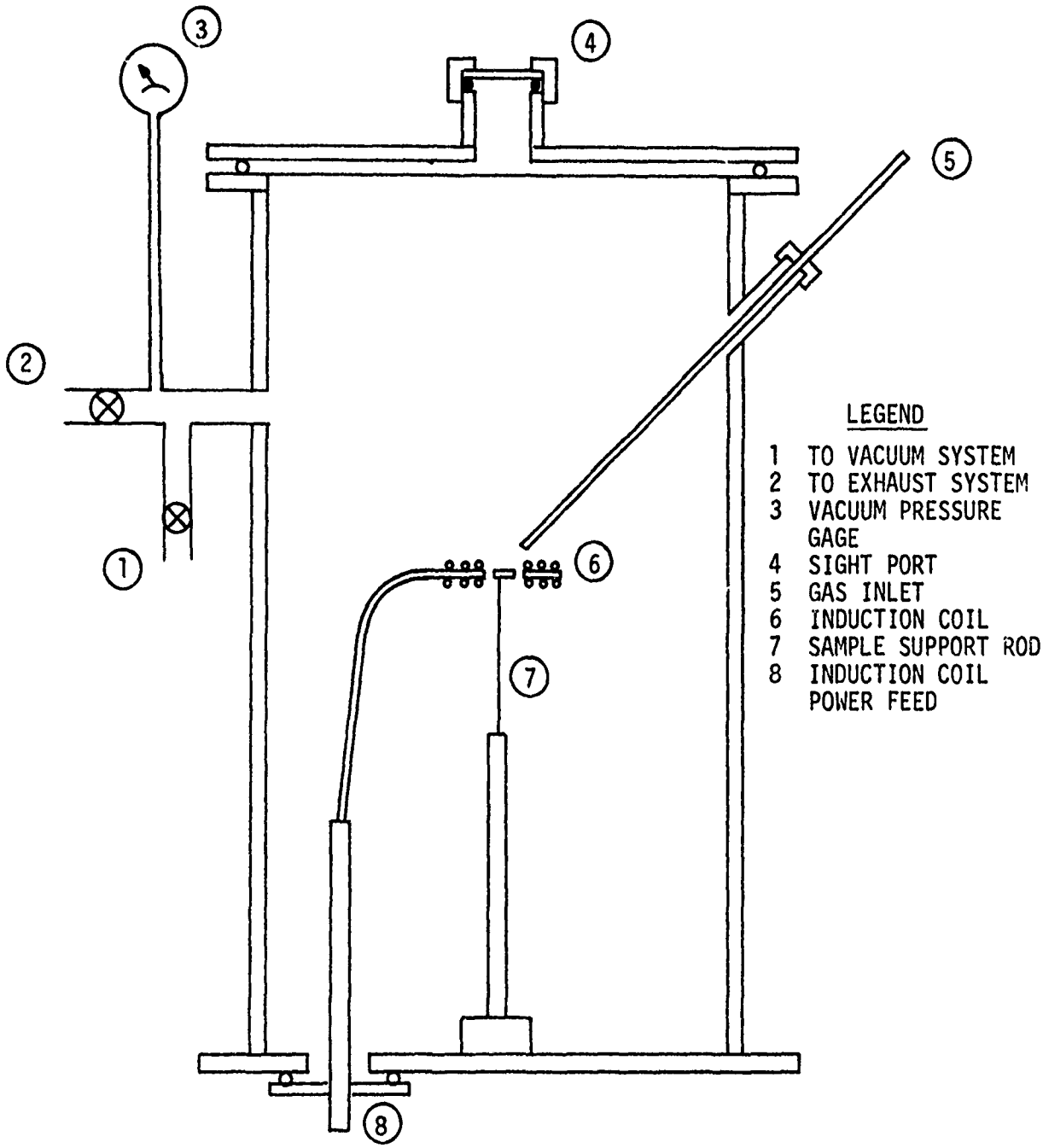

Figure 1. Schematic Diagram of Refractory Metals/Fluorine Reaction Chamber

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

The following conditions for corrosion tests were constant during most of the tests: (1) nozzle distance, 1 in.; (2) total gas flow rate, 10 ft^3/hr; (3) exposure time, 5 min; and (4) nozzle exit velocity, 400 ft/sec. Deviations were made only in specific cases where the effects of variations were examined. The test procedure was constant for the various corrosion tests. Test samples were heated to the exposure temperature with only the argon flowing. After stabilization of the sample temperature, the fluorine was introduced. Normally, this did not result in significant variation of the sample temperature as argon represented the major portion of the gas stream. In some cases, it was necessary to reduce the exposure time to 3 min or increase exposure time up to 10 min to obtain total weight losses of an amount required for recession rate calculations.

The surface recession rates were calculated from weight loss of the 0.5 x 0.125-in. (nominal) thick test samples, assuming a linear time dependence of the weight loss. The effective surface area was obtained using one of the 0.5 x 0.5-in. surfaces (location of direct gas impingement) and the four 0.5 x 0.125-in. edges of the test sample. This is consistent with the observed location of attack on all test samples. Attack of the corrodent gases was usually not uniform over the test sample; material removed was maximum at the center of the 0.5 x 0.5-in. surface where direct gas impingement occurred. Thus, test samples tended to have a concave top surface after exposure. This concave top surface is described as "cratering".

The effect or nozzle distance on the surface recession of tungsten in argon-6.5 vol% fluorine at 4000°F is summarized in Table IV and plotted in Figure 2. These data show that corrosion rate increases with decreasing nozzle distance but varies only a minor amount for nozzle distances of around 1 in. At the 1 in. nozzle distance the gas velocity across the sample surface is considered to be only slightly less than the nozzle exit velocity (400 ft/sec). Also plotted in Figure 2 are the maximum recession rates obtained by micrometer measurements of the minimum thickness of the test samples after exposure. Note that the "cratering" increases rapidly at distances less than 1.5 in.

The effects of fluorine flow rate, velocity, and concentration on the corrosion rate of tungsten in fluorine-argon mixtures were determined at 4000°F. The pertinent data are summarized in Table V and plotted in Figures 3, 4, and 5. These data show that the corrosion rate is dominantly dependent upon the fluorine flow rate rather than either velocity or concentration, although the latter effects may not be negligible. This suggests that the corrosion rate is not controlled by reaction rates but rather by mass transport conditions at this high temperature.

TABLE IV

EFFECT OF NOZZLE DISTANCE ON THE CORROSION RATE OF TUNGSTEN IN A FLUORINE-ARGON MIXTURE (6.5/93.5 VOL) AT 4000°F* (Ref. 5)

Nozzle Distance, in.	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min	Maximum Measured Surface Recession, mils/min
0.75	140.0	2.86	9.3
1.0	128.6	2.62	6.8
1.25	130.5	2.66	6.2
1.25	137.0	2.79	6.3
1.5	119.5	2.44	4.6
1.75	109.0	2.22	3.8
1.75	120.5	2.46	4.3
2.5	109.0	2.22	3.0
3.0	90.5	1.83	2.5
3.0	94.5	1.93	2.4

*Total gas flow rate, 10 ft^3/hr; fluorine flow rate, 0.65 ft^3/hr; nozzle exit velocity ∿400 ft/sec. Specimen oriented ∿45° to gas stream.

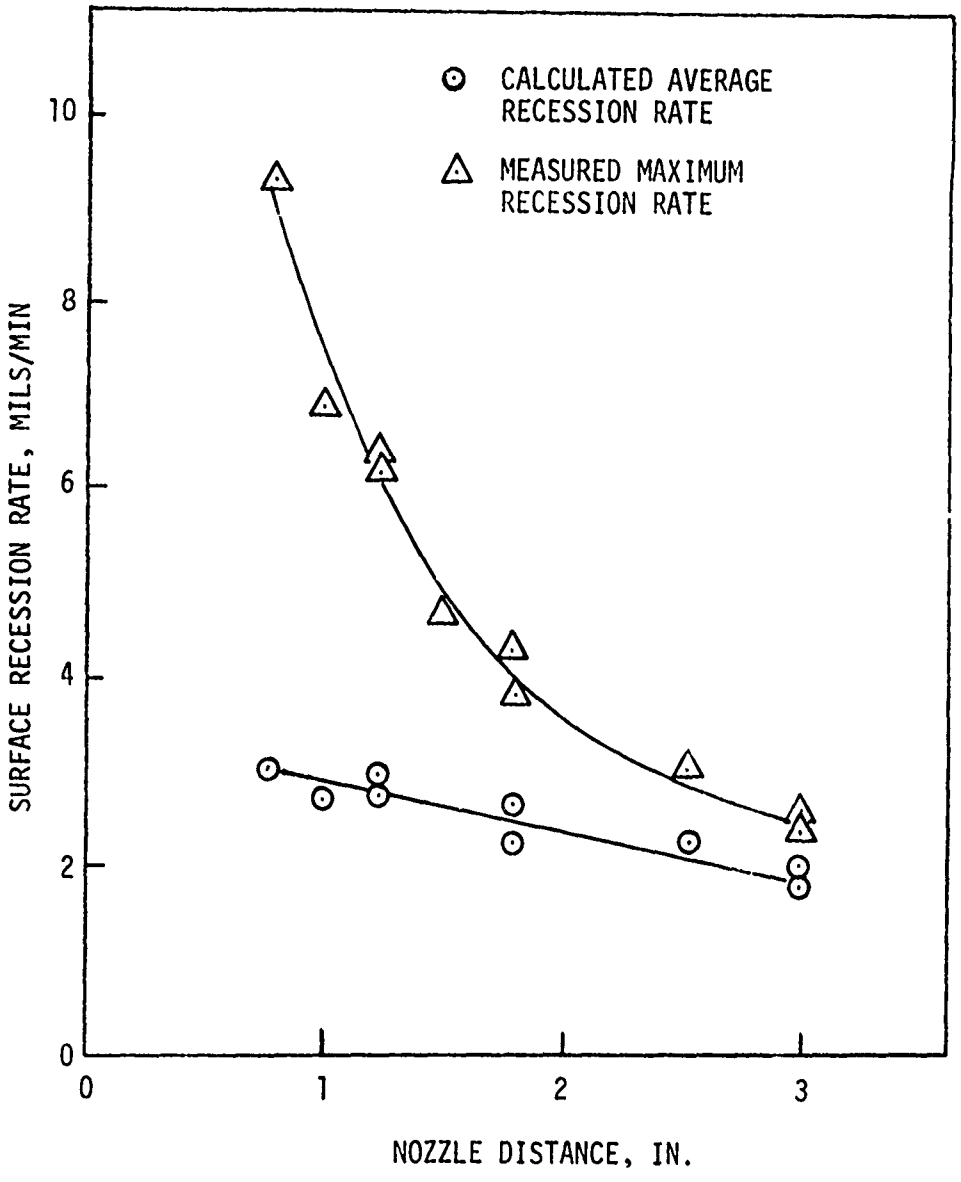

Figure 2. Effect of Nozzle Distance on the Corrosion Rate of Tungsten at 4000°F in Fluorine-Argon Mixture (6.5/93.5 vol)

TABLE V

EFFECT OF FLUORINE FLOW RATE, VELOCITY, AND CONCENTRATION ON THE CORROSION RATE OF TUNGSTEN IN FLUORINE-ARGON MIXTURES AT 4000°F (Ref. 5)

Total Flow Rate, ft^3/hr	Fluorine Flow Rate, ft^3/hr	Fluorine Content, % vol	Nozzle Exit Velocity, ft/sec	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min
2.5	0.65	26	98	115.0	2.34
4	0.26	6.5	157	50.6	1.03
5	0.65	13.0	196	120.0	2.45
8	0.52	6.5	314	101.0	2.06
10	0.25	2.5	393	47.6	0.97
10	0.65	6.5	393	128.6	2.62
10	1.0	10.0	393	186.5	3.80
12.5	0.65	5.2	491	139.0	2.83
12.5	0.25	2.0	491	51.5	1.05
12.5	0.81	6.5	491	152.0	3.10
12.5	1.0	8.0	491	191.0	3.90

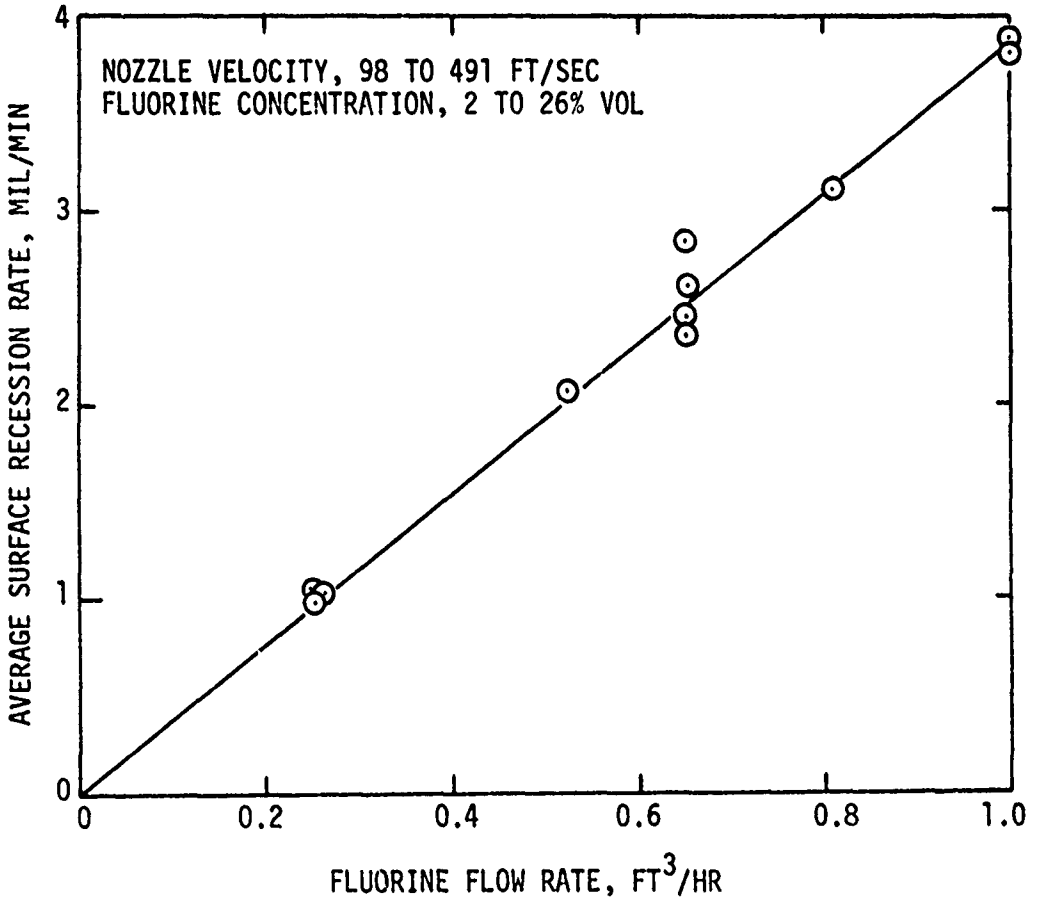

Figure 3. Effect of Fluorine Flow Rate on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

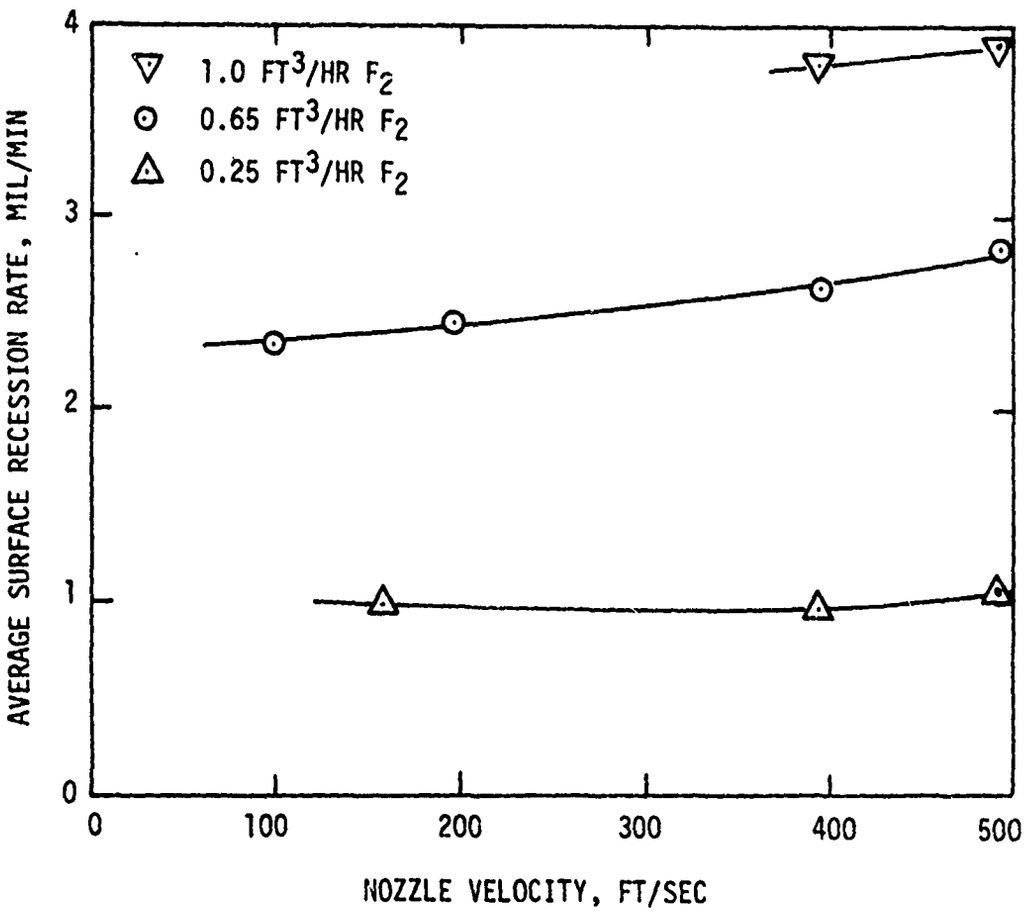

Figure 4. Effect of Nozzle Velocity on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

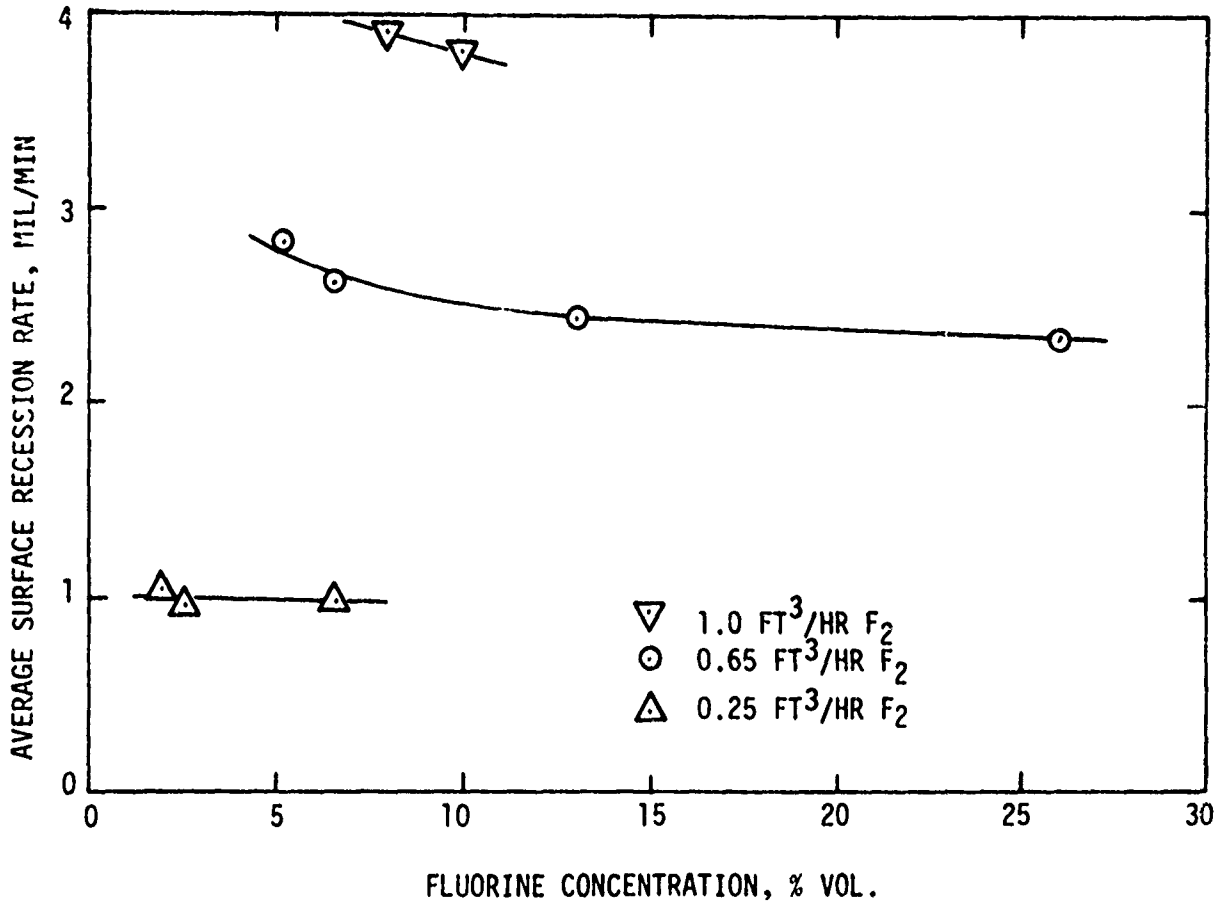

Figure 5. Effect of Fluorine Concentration on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

The effect of temperature on the corrosion rate of tungsten under various flow conditions was studied to obtain insight into the possible corrosion mechanism. The pertinent data are summarized in Table VI and shown graphically in Figure 6. It can be seen in Figure 6 that the curves all have the same general shape and that corrosion rates decrease quite rapidly at approximately 4700 to 5000°F. This decrease is attributed to the thermal instability of the tungsten/fluorine reaction products at temperatures within that range. That apparent basis for decreased corrosion rates is strengthened by the observation that tungsten hexafluoride, WF_6, in contact with tungsten shows markedly decreasing tungsten surface recession rates at about 4500°F. This is most directly reconciled by the dissociation of WF_6 (or a lower fluoride) to solid tungsten and fluorine.

TABLE VI

EFFECT OF NOZZLE-SPECIMEN DISTANCE AND TEMPERATURE ON THE CORROSION RATE OF TUNGSTEN IN A FLUORINE-ARGON MIXTURE (6.5/93.5 VOL)

Nozzle Distance, in.	Specimen Temperature, °F	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min
1	3000	121.5	2.48
1	3500	126.4	2.58
1	3500	128.6	2.63
1	4000	128.8	2.62
1	4580	124.8	2.54
1	5110	92.0	1.88
1	5500	55.2	1.13
1	5800	30.6	0.62
3	4000	90.3	1.84
3	5000	71.0	1.45
*	4000	16.8	0.34
*	5000	10.8	0.22
*	5280	4.5	0.09

*Nozzle baffled to avoid direct impingement of gas mixture on the sample.

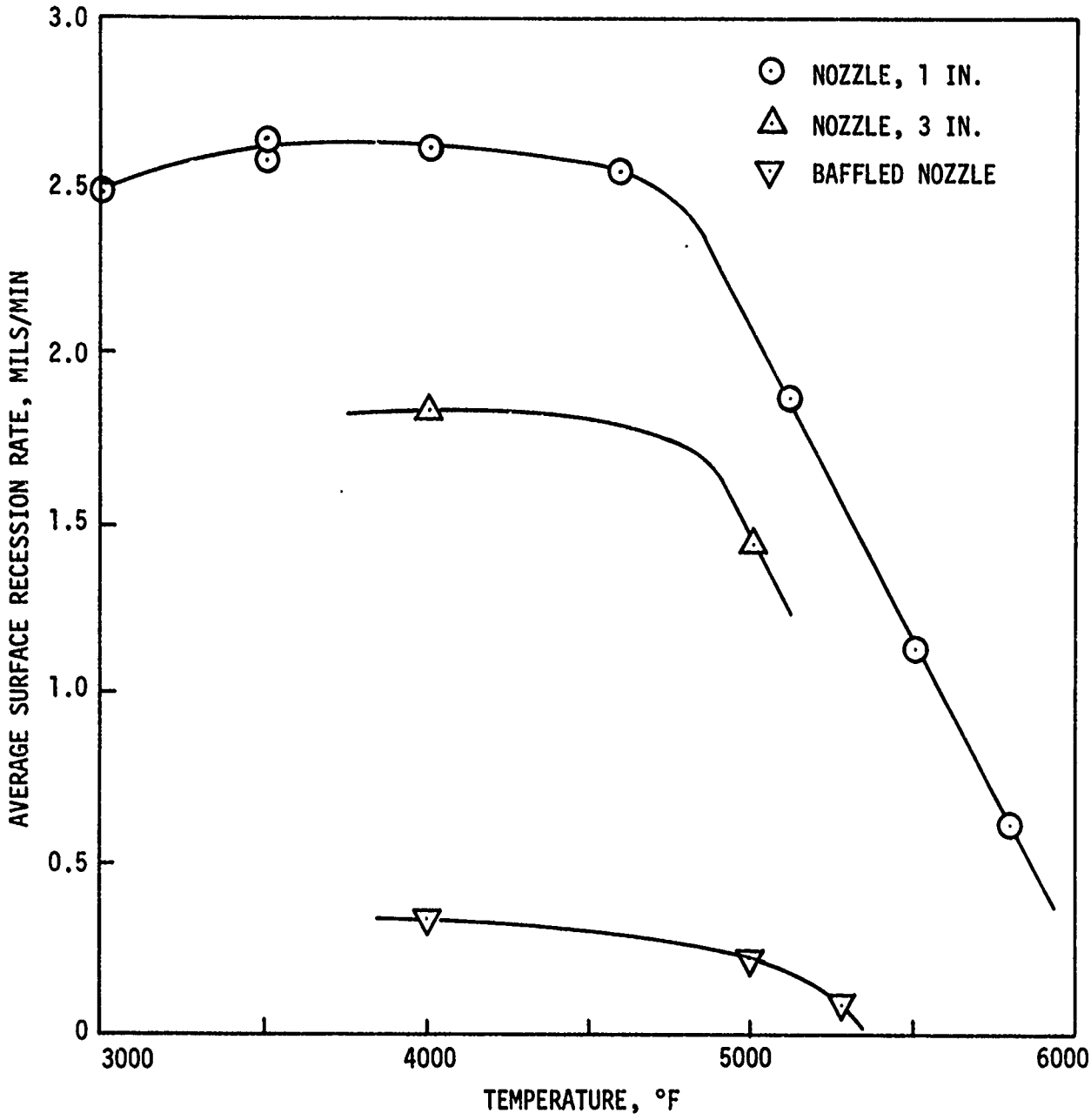

Figure 6. Effect of Temperature and Flow Conditions on the Corrosion Rates of Tungsten in a Fluorine-Argon Gas Mixture (6.5/93.5 vol)

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

A summary of the corrosion rate data obtained with fluorine-argon gas mixtures and tantalum, tungsten, tungsten-base alloys, rhenium-base alloys, and iridium and iridium-base alloys is given in Tables 7, 8, 9, 10, and 11, respectively. Representative data from these tables are graphically displayed in Figure 7 for the 6.5/93.5 vol fluorine-argon gas mixture. It is interesting to note that the metals appear to be corroded at about the same rates at 2500°F but differ very substantially at higher temperatures. Each material begins to show a rapidly decreasing corrosion at some high temperature and that temperature would appear to represent the temperature at which the metal fluoride shows an appreciable tendency to dissociate.

TABLE VII

CORROSION RATE OF TANTALUM IN FLOWING FLUORINE-ARGON MIXTURES (*)

Specimen Temp., °F	F_2 Conc., % Vol.	Average Specific Weight Loss, mg/cm^2/min	Average Specific Surface Recession, mils/min	Ref.
4000	2.5	53.2	1.26	4
5000	2.5	58.4	1.38	4
4000	6.5	144.8	3.44	4
5000	6.5	137.0	3.25	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ∿400 ft/sec. Specimen 1 in. from nozzle at ∿45° to gas stream.

TABLE VIII

CORROSION RATE OF TUNGSTEN IN FLOWING FLUORINE-ARGON MIXTURES*

Specimen Temp., °F**	F_2 Conc., % vol	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min	Ref.
5110	0.4	5.6	0.12	4
3550	2.5	52.8	1.07	4
4000	2.5	47.6	0.97	4
4580	2.5	42.5	0.87	4
5110	2.5	27.1	0.55	4
5110	2.5	28.8	0.55	4
2225	6.5	106.5	2.17	5
2380	6.5	103.2	2.11	5
2390	6.5	100.0	2.04	5
2830	6.5	121.2	2.47	5
3000	6.5	121.5	2.48	5,6
3500	6.5	126.4	2.58	4,5,6
3500	6.5	128.6	2.63	4
4000	6.5	128.8	2.62	5,6
4580	6.5	124.8	2.54	5,6
4580	6.5	124.8	2.54	4
5110	6.5	92.0	1.88	4,5
5500	6.5	55.2	1.13	6
5800	6.5	30.6	0.62	6
3500	10.0	195.0	4.00	4
4000	10.0	186.5	3.80	5
4580	10.0	169.0	3.45	4
5110	10.0	142.4	2.90	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ∿400 ft/sec. Specimen 1 in. from nozzle at ∿45° to gas stream.

**Emittance of 0.35 used in optical temperature correction.

TABLE IX

CORROSION RATES OF TUNGSTEN-BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

I. Tungsten-Rhenium (74/26 wt)

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, mg/cm^2/min	Average Surface Recession Rate, mil/min	Ref.
4000	2.5	47.2	0.94	4
4500	2.5	40.0	0.80	4
5000	2.5	40.2	0.80	4
4000	6.5	113.2	2.25	4
4500	6.5	102.0	2.03	4
5000	6.5	91.0	1.81	4
4000	10.0	163.2	3.25	4
4500	10.0	151.0	3.01	4
5000	10.0	132.6	2.63	4

II. Tungsten-Iridium (95/5 wt)

3500	6.5	104.5	2.12	5
4000	6.5	109.0	2.22	5
4500	6.5	103.5	2.11	5
4660	6.5	110.0	2.23	5
5000	6.5	106.0	2.15	5

III. Tungsten-Iridium (90/10 wt)

3500	6.5	103.8	2.09	5
4000	6.5	98.5	1.98	5
4500	6.5	96.0	1.93	5
4660	6.5	97.5	1.96	5
5000	6.5	89.5	1.80	5

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ~400 ft/sec. Specimen 1 in. from nozzle at ~45° to gas stream.

TABLE X

CORROSION RATES OF RHENIUM AND RHENIUM-BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, mg/cm^2/min	Average Surface Recession Rate, mil/min	Ref.
I. Rhenium				
5000	2.5	4.0	0.07	4
2500	6.5	119.5	2.24	6
2500	6.5	119.0	2.24	6
3000	6.5	119.0	2.22	5,6
3500	6.5	123.0	2.30	5,6
4000	6.5	87.6	1.64	4,6
4000	6.5	73.2	1.37	4,5,6
4500	6.5	61.9	1.16	4,5,6
4500	6.5	45.2	0.85	4,5,6
5000	6.5	23.0	0.43	4,5,6
5000	6.5	18.0	0.33	5,6
5200	6.5	28.3	0.53	6
4000	10.0	150.0	2.72	4
5000	10.0	42.2	0.79	4
II. Rhenium-Iridium (85/15 wt)				
4000	6.5	90.0	1.67	5
4500	6.5	69.2	1.27	5
4840	6.5	43.3	0.81	5
4500	10.0	75.6	1.4	5
5000	10.0	59.5	1.10	5
III. Rhenium-Iridium (75/25 wt)				
4000	6.5	81.5	1.50	5
4500	6.5	60.6	1.11	5
5000	6.5	30.3	0.56	5
4500	10.0	69.4	1.28	5
5000	10.0	43.8	0.81	5
IV. Rhenium-Iridium (65/35 wt)				
4000	6.5	71.0	1.30	5
4500	6.5	52.9	0.96	5
5000	6.5	26.8	0.47	5
4500	10.0	58.2	1.06	5
5000	10.0	41.5	0.75	5

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ∿400 ft/sec. Specimen 1 in. from nozzle at ∿45° to gas stream.

TABLE XI

CORROSION RATES OF IRIDIUM AND IRIDIUM BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

I. Iridium

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, mg/cm²/min	Average Surface Recession Rate, mil/min	Ref.
2500	6.5	131.0	2.29	5,6
2730	6.5	105.0	1.84	5,6
3000	6.5	78.0	1.36	5,6
3000	6.5	68.0	1.19	6
3000	6.5	65.5	1.15	5,6
3500	6.5	29.4	0.51	4,6
3500	6.5	22.4	0.39	4
3500	6.5	18.7	0.33	5,6
4000	6.5	15.3	0.27	5,6
4000	6.5	11.2	0.20	4
4370	6.5	12.8	0.22	4
4400	6.5	10.2	0.18	4,6
4000	10.0	21.7	0.38	4

II. Iridium-Rhenium (67/33 wt)

4000	2.5	13.1	0.23	4
4425	2.5	11.2	0.20	4
2680	6.5	105.6	1.89	6
3060	6.5	70.6	1.27	6
3500	6.5	47.0	0.84	4
3500	6.5	46.0	0.82	6
3500	6.5	43.0	0.77	5,6
4000	6.5	29.3	0.53	4,6
4000	6.5	18.9	0.34	5,6
4420	6.5	16.0	0.29	6
4425	6.5	16.0	0.29	4
4500	6.5	13.3	0.24	5,6
4700	6.5	13.2	0.23	4
4000	10.0	46.0	0.82	4
4425	10.0	37.0	0.66	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ∿400 ft/sec. Specimen 1 in. from nozzle at ∿45° to gas stream.

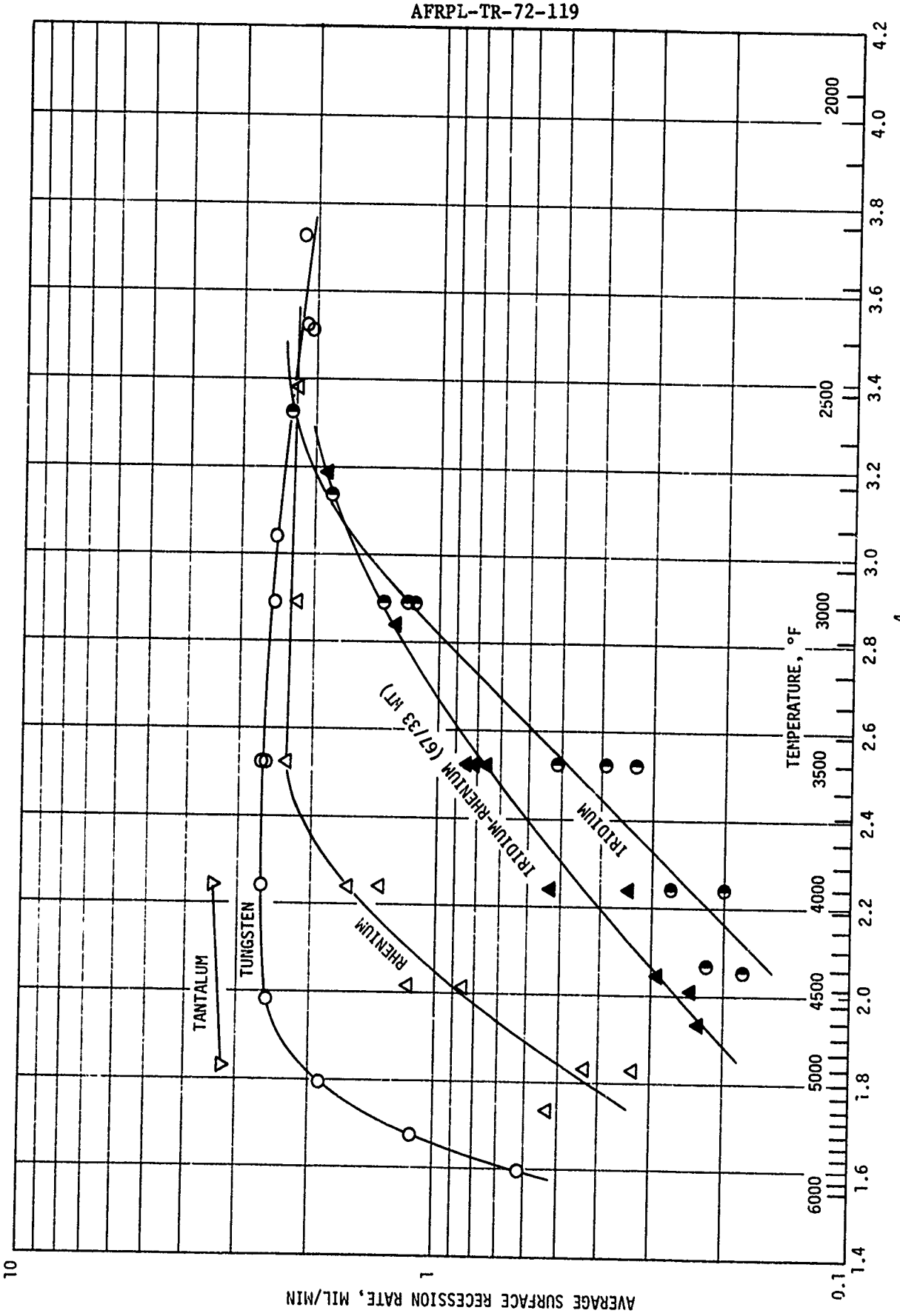

Figure 7. Corrosion Rates of Refractory Metals in Flowing Fluorine-Argon Gas Mixtures (6.5/93.5 Vol.)

SECTION III

METALS RESPONSE TO LIQUID FLUORINE FLOW AND IMPACT

A. LIQUID IMPACT ON HEATED METALS

Under Contract F04611-72-C-0031, Dynamic Compatibility of Halogen Propellants (Reference 1), the Aerojet Liquid Rocket Company conducted flow tests in which liquid fluorine was impacted on heated specimens of twelve metals. The metal investigated were:

304-L Stainless Steel	6061-T6 Aluminum
301 Stainless Steel	2219 Aluminum
301 Cryo Stainless Steel	OFHC Copper
347 Stainless Steel	Inconel 718
321 Stainless Steel	Monel K-500
A-286 Stainless Steel	Nickel 200

The test apparatus consisted of two major components: (1) a liquid feed system and (2) an electrical-resistance heating system for the metal specimens. The temperature of the metal specimens was measured by means of thermocouples attached to the back of the metal strip which was 0.010-in. thick. The metal specimens were placed within 3/16 in. of the discharge orifice of the liquid feed system. The orifice diameter of the system was 0.015 in. and the entire feed system was temperature conditioned to -320°F. For each test, a fresh, clean, unpassivated metal specimen was used and the temperature level was increased in 100°F increments in the presence of air for each test until the impacting liquid propellant caused the metal specimen to burn. The temperature below which significant attack no longer occurred was determined within $\pm$50°F. Until the ignition temperature was reached, there was only slight evidence of attack on the metal surfaces. The data are presented in Table XII.

Recognizing that the threshold temperatures given in Table XII are accurate to within only about $\pm$50°F, it would appear that the velocity of impingement generally has a weak influence on threshold temperatures with few exceptions. For example, the apparent velocity effect on threshold temperatures is greater than 150°F for more than a two-fold change in velocity on only certain of the stainless steels, i.e., 301, 321, and 304-L.

Comparing the nonignition threshold temperatures in Table XII for liquid impingement with the high-probability-of-failure threshold temperatures in Table II for flowing gas shows that both tests lead to virtually identical material rankings. Further comparisons show that aluminum, copper, and the stainless steels appear to have appreciably lower threshold temperatures to high velocity liquid impingement than to sonic gas flow. Again comparing Table XII and Table II data, a first glance would suggest that Inconel 718,

TABLE XII

MAXIMUM TEMPERATURES OF METAL SURFACES ON WHICH IMPACTING STREAMS OF LIQUID FLUORINE DO NOT RESULT IN IGNITION

Material	Approximate Nonignition Threshold Temperature, °F		
	LF_2 Velocity of 130 ft/sec	LF_2 Velocity of 240 ft/sec	LF_2 Velocity of 295 ft/sec
6061-T6 Aluminum	850*		
2219 Aluminum	850*	850*	
OFHC Copper	1150	1050	
301 Stainless Steel	1450	1100	1100
347 Stainless Steel	1300	1200	1300
321 Stainless Steel	1550	1550	1350
304-L Stainless Steel	1650	1650	1350
301 Cryo Stainless Steel	1550	1400	1400
A-286 Stainless Steel	1650	1600	1550
Inconel 718	1950	1850	1850
Monel K-500	1950	2000	2100
Nickel 200	2150	2100	2200

*Temperatures at which specimen would occasionally burn in air.

III, A, Liquid Impact on Heated Metals (cont.)

Monel K-500, and Nickel 200 are more resistant to impinging liquid fluorine than to sonic gas flow. However, the thresholds in Table II for these materials refer to a potential failure mode involving the onset of strong exotherms and the buildup of significant films of corrosion products only. No evidence of ignition was obtained in flowing sonic gas through Inconel 718, Monel K-500, and Nickel 200 even though pulse temperatures near 2400°F were observed.

B. LIQUID FLOW THROUGH AND IMPACT ON METALS AT LOW TEMPERATURES

Schmidt (Reference 7) has reported the results of tests in which specimens of various metals in selected geometric configurations were exposed to liquid fluorine under controlled conditions of flow and pressure. None of the metal samples eroded, decomposed, or exhibited any measurable physical or chemical changes. In a run made with a Teflon sample, instantaneous chemical reaction and decomposition occurred.

Fluorine was forced through 0.0135-in. ID metal orifices with pressures up to 1500 psi and velocities up to 376 ft/sec; the maximum cumulative flow time per specimen was 1 hr and the minimum was 22 min. Larger orifices were subjected to even higher velocities (over 400 ft/sec) for periods up to 60 sec. Only a slight yellowish color appeared on the upstream side of nickel and aluminum orifices. A brass orifice appeared slightly darker, and stainless steel appeared etched.

Impact plates of stainless-steel weld slag and aluminum sustained fluorine environments with pressures from 100 to 1350 psi and velocities from 136 to 355 ft/sec for nearly 60 sec without effects other than slight discoloration. No reaction was produced by sharpedged turbulence test wedges of stainless steel, aluminum, and brass at velocities up to 169 ft/sec.

The results of this investigation show that turbulence, fluid friction, and impact effects resulting from high-pressure, high-velocity liquid-fluorine flow through clean tubing or past irregularly shaped or sharpedged objects are not likely to initiate fluorine-system failures at low temperatures. The successful operations achieved in this series of compatibility tests can be attributed to the meticulous care that has taken in the assembly, cleaning, and passivation techniques used before exposure of the system to severe dynamic fluorine service. Therefore, improper choice of hardware, poor assembly techniques, and inadequate cleaning and pickling procedures appear to be the primary cause of fluorine-system failures. The results of these tests are summarized in Table XIII.

In related studies at Douglas Aircraft Company (Reference 8), experiments were conducted to evaluate the erosion and impingement resistance of aluminum-silicon alloy, A356-T6, in LF_2 (0.02 vol% HF). This was

TABLE XIII

COMPATIBILITY OF METALS WITH LIQUID FLUORINE UNDER HIGH VELOCITY FLOW AND IMPACT CONDITIONS

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Leak-simulator orifice 0.0135-in. ID, L/D = 27.75	Aluminum (24 ST)	525	377	9.64	528	0.0183	184	Slight yellowish discoloration on upstream side of orifice
		1012	864	9.64	340	0.0283	293	
		1500	1432	12.43	436*	0.0285	287	
		1460	1436	15.25	424	0.0360	372	
		1339	1339	15.25	432	0.0353	365	
				62.21	2160 (36 min)			
	Stainless steel (347)	1386	1226	17.7	616*	0.0287	297	Slight frosted or etched effect on upstream side. Less affected on downstream side.
		1390	1206	17.7	578	0.0306	317	
		1500	1375	13.85	518*	0.0267	276	
		1510	1350	13.85	488	0.0284	293	
		1505	1443	13.85	472	0.0294	303	
		1512	1408	13.85	480	0.0289	299	
		1500	1398	13.85	500	0.0277	286	
				104.65	3652 (60.9 min)			
	Brass (64 SE)	1495	1395	12.43	344	0.036	376	
		1500	1390	15.25	670*	0.023	235	Slightly darker after exposure
		1465	1424	15.25	440	0.035	358	
				42.93	1454 (21.9 min)			
	Nickel	1100	1015	11.92	696*	0.01713	177	Slight yellowish discoloration on upstream side
		1413	1336	11.92	616*	0.01935	200	
				23.84	1312 (21.9 min)			

*Orifice clogged

Table XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Leak-simulator orifice; 0.025-in. ID, L/D = 5	Aluminum (soft)	1453	1315	17.7	132	0.134	417	
		1465	1360	17.7	130	0.136	410	
		1486	1302	13.85	110	0.126	380	Slight frosted appearance on both sides
		1500	1282	13.85	110	0.126	379	
		1495	1326	13.85	107	0.130	390	
		1492	1391	13.85	108	0.128	386	
		1505	1375	13.85	106	0.131	394	
				104.65	803 (13.4 min)			
Sharp-edged orifice; 1/8-in. ID	Aluminum (soft)	785	505	10.45	6.8	1.54	185	
		1480	1203	10.45	4.4	2.38	286	
		1465	1169	10.45	4.6	2.27	273	Slightly coated on downstream side; frosty appearance.
		1440	1144	10.45	4.6	2.27	273	
		1452	1159	10.45	4.0	2.61	315	
		1465	1196	10.45	4.6	2.27	273	Slightly etched on upstream side
		1470	1192	10.45	4.0	2.61	315	
				73.15	33.0			
	Brass (64 SE)	1008	773	9.74	5.7	1.71	206	
		1482	1206	9.74	4.9	1.99	240	
		1505	1249	9.74	4.2	2.32	279	
		1498	1226	9.74	4.5	2.16	261	
		1504	1223	9.74	4.8	2.03	245	
		1494	1232	9.74	4.7	2.07	249	Purple discoloration on downstream side of orifice
		1500	1223	9.74	4.8	2.03	244	
		1493	1233	9.74	4.4	2.21	267	
		1450	1190	9.74	4.7	2.07	249	
		1485	1334	9.74	4.4	2.21	266	
		1500	1358	9.74	4.0	2.43	266	
				107.14	51.1			

TABLE XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Sharp-edged orifice; 1/8-in. ID (cont.)	Stainless steel (304)	85	85	9.97	20.5	0.485	58.4	
		121	114	9.97	16.0	0.622	74.9	
		300	278	9.97	9.0	1.108	133.3	
		408	391	9.97	9.1	1.095	131.8	
		1005	811	9.97	6.0	1.66	200.0	
		1202	990	9.97	5.44	1.83	220.0	
				59.82	66.04 (1.1 min)			
Impact Plate with Round-edged orifice; 1/8-in. ID	Stainless steel weld slag (304)	1344	1206	11.92	3.78	3.17	355	
		1500	1362	11.92	4.5	2.65	349	
		102	85	9.74	8.6	1.13	136	Very slight etched effect but no apparent attack on impact sample. Slight yellowish discoloration on upstream side of orifice.
		1000	704	9.74	5.8	2.12	201	
		1475	1170	9.74	4.2	2.32	279	
		1485	1173	9.74	4.4	2.21	280	
		1480	1219	9.74	3.3	2.95	350	
		1471	1168	9.74	4.6	2.12	280	
		1495	1196	9.74	4.5	2.16	282	
		1480	1176	9.74	4.0	2.43	293	
		1495	1183	9.74	4.2	2.32	284	
		1490	1337	9.74	3.9	2.50	301	
		1500	1349	9.74	4.0	2.43	293	
				130.98	57.8			
	Aluminum (soft)	800	568	10.45	5.88	1.78	214	
		1470	1195	10.45	4.2	2.49	299	Slight etched effect on impact sample
		1475	1172	10.45	4.8	2.18	262	
		1470	1180	10.45	4.6	2.27	273	
	Stainless steel (304)	1465	1165	10.45	4.4	2.38	286	No effect on orifice except slight bluish cast on downstream side
		1455	1169	10.45	4.3	2.43	293	
		1460	1167	10.45	4.6	2.27	273	
				73.15	32.8			

TABLE XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
							Cycles per second*	
Rotating-vane flowmeter, ball-bearing (stainless steel rotor)	Stainless steel (316, 420, 430, 440)	85	--	9.97	20.5	0.465	46.5	Rotor-mount retainer rings slightly eroded and loose; would have affected running on continued operation.
		121	--	9.97	16.0	0.622	61.5	
		300	--	9.97	9.0	1.108	93.0	
		408	--	9.97	9.1	1.095	109.5	
		1005	--	9.97	6.0	1.66	165.0	
		1202		9.97	5.44	1.83	183.0	
				59.82	66.04 (1.1 min)			
	Aluminum (soft)	1443	1200	16.35	0.7	23.4	155.0	All four sides of sample had sooty film or coating. Not adherent; rubbed off easily. Did not seem to be in metal surface but on it; metal underneath was unchanged.
		1260	761	16.35	3.14	5.2	34.4	
		1370	872	16.35	3.10	5.3	39.4	
		1295	921	16.35	1.96	8.3	54.0	
		1360	873	16.35	2.75	5.9	39.5	
		1295	1057	10.20	0.58	17.6	117.0	
		1357	1067	10.20	0.67	17.9	118.0	
		1391	1103	10.20	0.40	25.5	169.0	
				112.35	13.20			
	Teflon	50	50	--	--	--	--	Immediate ignition on contact.

*100 cycles ~ 1 lb liquid fluorine.

TABLE XIII (cont.)

Configuration	Material	Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Reynolds Number, Re	Remarks
1/4-in. tubing; 0.1285-in. ID, length = 11.3 ft	Stainless steel (304)	0-120*	115	11.0	68.8	0.16	17.4	88,000	All runs with 1/4-in. tubing made without liquid-nitrogen bath. Initial temperature, 75°F.
		0-420*	397	11.0	26.4	0.417	45.4	232,000	
		0-1017*	837	11.0	18.24	0.603	65.7	337,000	
		0-1505*	1297	11.0	14.64	0.751	81.7	543,000	
				44.0	128.08 (2.13 min)				
1/4-in. tubing; 0.182-in. ID, length = 12.2 ft	Aluminum (5052 SO)	0-133*	118	11.0	25.6	0.43	24.4	176,000	All runs with 1/4-in. tubing made without liquid-nitrogen bath. Initial temperature, 75°F.
		0-410*	385	11.0	22.0	0.50	28.4	205,000	
		0-1010*	768	11.0	12.0	0.917	52.0	377,000	
		0-1500*	1275	11.0	7.36	1.495	84.8	614,000	
		0-1485*	1312	11.0	7.16	1.536	87.3	632,000	
				55.0	74.12 (1.24 min)				
3/4-in. tubing	Stainless steel (304)	1260	--	16.35	3.14	5.2	17.8	526,000	The 3/4-in. tubing was part of the test apparatus
		1370	--	16.35	3.10	5.3	20.3	600,000	
		1360	--	16.35	2.75	5.9	20.4	602,000	
		1340	--	16.35	1.96	8.3	28.5	843,000	
		1340	--	16.35	1.26	13.0	44.5	1,315,000	
		1330	--	16.35	1.14	14.3	46.3	1,370,000	
		1319	--	16.35	1.0	16.4	55.8	1,650,000	
		1391	--	10.2	0.9	18.2	62.1	1,835,000	
			--	16.35	0.7	23.4	71.4	2,110,000	
			--	10.2	0.4	25.5	87.3	2,580,000	
Turbulence test wedge (sharp-edged)	Stainless steel (347)	1340	862	16.35	1.14	14.34	90.0		No effect
		1340	740	16.35	1.26	12.97	86.4		
		1330	886	16.35	1.0	16.35	108.5		
		1404	978	16.35	0.9	18.16	120.5		
				65.4	4.3				
	Brass (64 SE)	1319	800	10.2	0.9	11.3	70		Very slightly frosted appearance; slightly lighter in color than parent metal
		1383	1036	10.2	0.5	20.4	135		
		1286	1028	10.2	0.57	17.9	118		
		1346	1100	10.2	0.66	15.5	102		
				40.8	2.63				

*Instantaneous pressure release.

III, B, Liquid Flow Through and Impact on Metals at Low Temperatures (cont.)

accomplished by flowing LF_2 through an orifice test coupon and impinging on another test coupon 3/16 in. downstream. Orifice and impingement specimens were exposed to F_2 at -235°F for 30 min at velocities of 50 and 150 ft/sec. No orifice change was observed but superficial impingement attack was observed at both velocities.

The test conditions and the results of the individual runs are summarized in Table XIV.

TABLE XIV

COMPATIBILITY OF AN ALUMINUM-SILICON ALLOY WITH LIQUID FLUORINE UNDER HIGH VELOCITY FLOW AND IMPACT CONDITIONS*

Material	Velocity, ft/sec	Orifice Diameter, in. Initial	Orifice Diameter, in. Final	Final Condition of Impingement Coupon
Al A356-T6 NASA Grade IIIF	50	0.065	0.065	Superficial attack
Al A356-T6 NASA Grade IIIF	150	0.039	0.039	Superficial attack

*LF_2 temperature, -235°F: LF_2 static pressure, 400 psig; flow rate, 0.50 gal/min; test time, 30 min.

SECTION IV

IV. METALS BEHAVIOR IN THE PRESENCE OF FLUORINE ADIABATIC COMPRESSION

As part of the program on the dynamic compatibility of halogen propellants with metals, Contract F04611-72-C-0031 (Reference 1), the Aerojet Liquid Rocket Company conducted adiabatic compression tests on gaseous fluorine in the presence of metals. The metal specimens used in the investigation were composed of the following alloys:

304-L Stainless Steel	6061-T6 Aluminum
347 Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
	Nickel 200

The purpose of the tests was to determine the maximum allowable conditions of adiabatic compression of gaseous fluorine that can be tolerated in systems containing the metals listed above.

The apparatus used in the investigation was a U-tube adiabatic compression test apparatus which was modified to accommodate the introduction of gaseous halogen propellants and metal specimens and to incorporate a means of temperature conditioning the loaded U-tube. A schematic diagram of the apparatus is shown in Figure 8. The test specimen holder was a 1/4-in. solid AN plug used to seal the end of the U-tube. The test specimen was a strip of metal sheet 0.010-in. thick by 0.10-in. wide by 0.10-in. long which was spot welded to the end of the AN plug. The U-tube was fabricated from Inconcel X-750 1/4-in. tubing approximately 16-in. long.

The tests were conducted in the following manner. The U-tube was attached to the apparatus and the specimen holder used to seal the open-end of the U-tube. The tube was then evacuated to 1 torr or less, temperature conditioned, and then 15.7 psia of gaseous fluorine was gradually introduced into the assembly. The fluorine was allowed to remain in the U-tube for five minutes prior to the test to allow for initial passivation of the metal. The pneumatic line valve was then actuated and the nitrogen from the accumulator tank used to compress the fluorine vapor. The U-tube assembly was then vented and flushed with nitrogen and the test specimen was examined visually to ascertain if any attack occurred. Microscopic examination was used to evaluate the samples which were not totally consumed in the test. A 1000 lb burst disc made of 304-L stainless was used in each test to seal the pneumatic valve and check valve assembly from the halogen atmosphere prior to the test. The driving pressure in the accumulator tank and the initial fluorine temperature was varied with each material in order to define the pressures and temperatures at which the metals were susceptible to attack. The test specimen was replaced after each test to insure that comparable surfaces were being exposed to the test conditions. The pneumatic valve opened completely within 1.5 milliseconds and with an accumulator pressure of 1000 psia; the minimum pressurization rate was 6.7×10^5 psi/sec.

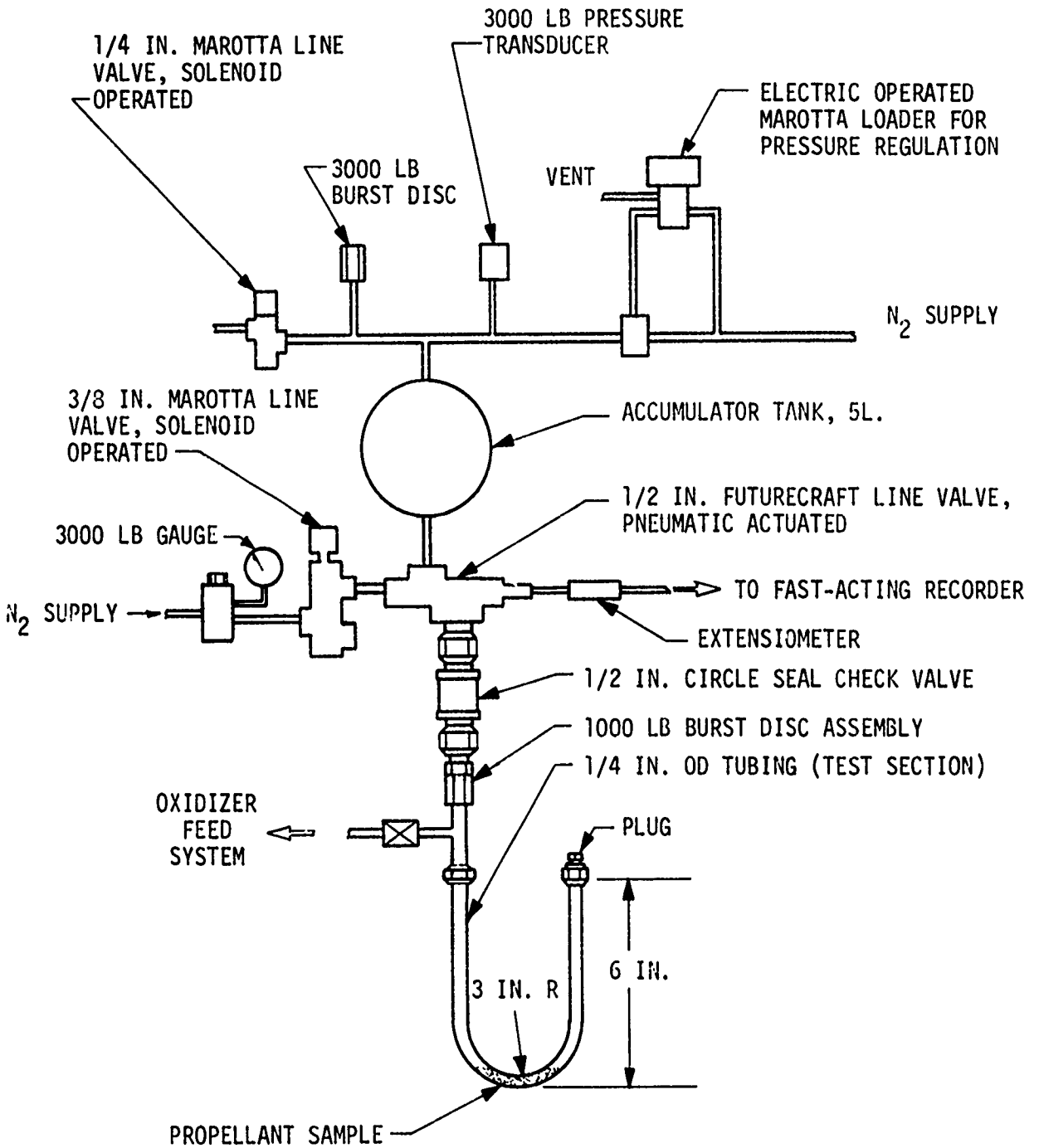

Figure 8. Schematic Diagram of U-tube Adiabatic Compression Apparatus

IV, Metals Behavior in the Presence of Fluorine Adiabatic Compression (cont.)

The results of 107 tests conducted on the specimens of the nine metals are summarized in Table XV. The initial fluorine temperature, T_o, and pressure, P_o, and the final pressure, P_f, are experimentally determined values. The final temperature, T_f, is calculated from Equation 1 assuming the fluorine to be a

$$T_f = T_o \left(\frac{P_f}{P_o}\right)^{\frac{\gamma-1}{\gamma}} \tag{1}$$

nondissociating ideal gas and where γ is defined by Equation 2 using values of Cp for fluorine from Reference 9.

$$\gamma = \frac{\left(\frac{Cp}{Cp - R}\right)_{T_o} + \left(\frac{Cp}{Cp - R}\right)_{T_f}}{2} \tag{2}$$

The estimated final density, ρ_f, is calculated from the perfect gas law and is evaluated at T_f and P_f. Test results denoted by a minus sign (-) indicate that attack is not evident by microscopic examination, those denoted by a single plus sign (+) indicate attack is apparent, and those denoted by a double plus sign (++) indicate the specimen was totally destroyed.

Specimens of OFHC copper and Nickel 200 were not visibly attacked under any of the test conditions. 304-L stainless steel and Inconel 718 were only slightly attacked. Monel K-500, 321 stainless steel, and A-286 stainless steel showed variable degrees of attack from superficial attack to total consumption. 347 stainless steel and 6061-T6 aluminum were totally consumed whenever attack was evident but each metal gave only one positive reaction out of 9 tests on each metal. The conditions under which the various metals can be expected to have approximately a 50% probability of reaction with gaseous fluorine subjected to adiabatic compression were derived from the data given in Table XV. These conditions are summarized in Table XVI. From the data presented in Tables XV and XVI, it is concluded that the metals can be ranked in categories in the following descending order of resistance to the effects of fluorine adiabatic compression: (1) Nickel 200 and OFHC copper, (2) Inconel 718, and (3) 304-L, 321 and A-286 stainless steels. The proper ranking of Monel K-500, 6061-T6 aluminum and 347 stainless steel is indefinite because of insufficient or irregular positive test results, but they appear to belong in the third category.

It is interesting to note that the results of these tests are in quite good agreement with gas flow and liquid impact data (see Tables II and XII, respectively) in terms of threshold temperatures and material rankings except that the adiabatic compression tests essentially reverse the order of Monel K-500 and OFHC copper. This significant reversal in relative resistance to attack has not been explained but it is also observed in connection with ignition temperatures in static fluorine (see Table III).

TABLE XV

BEHAVIOR OF VARIOUS METALS IN THE PRESENCE OF GASEOUS FLUORINE SUBJECTED TO ADIABATIC COMPRESSION

Metal	Initial Condition: Temp. T_o, °F	Initial Condition: Press., P_o, psia	Final Condition: Press., P_f, psia	Final Condition: Calc. Temp. T_f, °F	Final Condition: Est. Density, ρ_f, lb/ft^3	Test Results
304-L Stainless Steel	62	15.7	1515	1085	3.48	-
	67	15.7	2515	1275	5.14	-
	68	15.7	2815	1310	5.64	-,+
	67	15.7	3015	1335	5.95	+,+
	212	15.7	1015	1310	2.03	-,-
	212	15.7	1515	1470	2.78	-,+
	212	15.7	1765	1530	3.14	-,+
	212	15.7	2015	1585	3.49	+
	369	15.7	3015	2235	3.97	-
	370	15.7	3015	2235	3.97	-
321 Stainless Steel	66	15.7	3015	1330	5.97	-
	70	15.7	3015	1345	5.92	-,-,-,-
	212	15.7	915	1270	1.87	-,-
	212	15.7	1015	1310	2.03	-,-,+
	212	15.7	1265	1395	2.42	-.++
	212	15.7	1515	1470	2.78	-
	212	15.7	2015	1585	3.49	-,++
	212	15.7	2515	1685	4.16	++,++
	212	15.7	3015	1760	4.81	+,++,+
	374	15.7	3015	2250	3.94	-
	375	15.7	3015	2250	3.94	-
347 Stainless Steel	212	15.7	2015	1585	3.49	-,-,-
	212	15.7	2265	1635	3.83	-,-
	212	15.7	2515	1685	4.16	-,++
	360	15.7	3015	2205	4.01	-
	366	15.7	3015	2225	3.98	-
A-286 Stainless Steel	62	15.7	2515	1260	5.18	-
	62	15.7	2715	1290	5.50	-
	68	15.7	2815	1310	5.64	-,+,+
	67	15.7	3015	1335	5.95	++
	212	15.7	3015	1760	4.81	-,-
	331	15.7	3015	2120	4.14	-
	332	15.7	3015	2125	4.13	-
6061-T6 Aluminum	62	15.7	2015	1180	4.36	-
	62	15.7	2515	1260	5.18	-
	66	15.7	3015	1330	5.97	-,++,-
	212	15.7	3015	1760	4.81	-,-
	369	15.7	3015	2235	3.97	-
	370	15.7	3015	2235	3.97	-

TABLE XV (cont.)

BEHAVIOR OF VARIOUS METALS IN THE PRESENCE OF GASEOUS FLUORINE SUBJECTED TO ADIABATIC COMPRESSION (Cont.)

Metal	Initial Condition Temp. T_o, °F	Initial Condition Press., P_o, psia	Final Condition Press., P_f, psia	Final Condition Calc. Temp. T_f, °F	Final Condition Est. Density, ρ_f, lb/ft^3	Test Results
OFHC Copper	66	15.7	3015	1330	5.97	-
	70	15.7	3015	1345	5.92	-
	212	15.7	3015	1760	4.81	-,-
	367	15.7	3015	2230	3.97	-
	368	15.7	3015	2230	3.97	-
Inconel 718	62	15.7	3015	1325	5.99	-,-
	212	15.7	2265	1635	3.83	-,-
	212	15.7	2515	1685	4.16	-,+
	212	15.7	3015	1760	4.81	-,+,-,-
	358	15.7	3015	2200	4.02	-
	360	15.7	3015	2205	4.01	-
Monel K-500	66	15.7	2515	1275	5.14	-,-,+
	67	15.7	2715	1300	5.47	-
	67	15.7	2815	1310	5.64	-
	67	15.7	3015	1335	5.95	++
	212	15.7	2015	1585	3.49	-,-
	212	15.7	2515	1685	4.16	+,+
	212	15.7	3015	1760	4.81	-,-,-,-
	367	15.7	3015	2230	3.97	-
	368	15.7	3015	2230	3.97	-
Nickel 200	63	15.7	3015	1330	5.97	-,-
	212	15.7	2765	1720	4.50	-,-
	212	15.7	3015	1760	4.81	-,-
	361	15.7	3015	2210	4.00	-
	362	15.7	3015	2215	4.00	-

TABLE XVI

TERMINAL ADIABATIC COMPRESSION CONDITIONS THAT RESULT IN A 50% PROBABILITY OF FLUORINE/METAL REACTION

Metal	Conditions for a 50% Probability of Reaction: Calc. Final Temp., °F	Calc. Final Density, lb/ft^3	Magnitude of Resulting Reaction
6061-T6 Aluminum	∿1330*	∿5.97	Major
A-286 Stainless Steel	1300	5.57	Variable
304-L Stainless Steel	1310	5.64	Slight
	1500	2.96	Slight
321 Stainless Steel	1475	2.90	Variable
347 Stainless Steel	∿1685*	∿4.16*	Major
Inconel 718	∿1685*	∿4.16*	Slight
Monel K-500	1305	5.55	Variable
	∿1635	∿3.82	Slight
OFHC Copper	Not Defined		Insignificant
Nickel 200	Not Defined		Insignificant

*Insufficient positive reaction data points to define reaction probability accurately.

IV, Metals Behavior in the Presence of Fluorine Adiabatic Compression (cont.)

It can be seen in Table XV that no positive reactions were obtained when fluorine temperatures prior to adiabatic compression were in the temperature range of 331 to 375°F. The corresponding temperature and density conditions upon adiabatic compression were 2120 to 2250°F and approximately 4 lb/ft^3, respectively; conditions considerably more severe than those achieved in many positive tests which involved lower initial temperatures. The failure of specimens to react with fluorine under these apparently more drastic conditions has not been explained but it is postulated that passivation-type reactions at the highest initial temperatures may have resulted in the formation of "passive films" which are sufficiently protective to be affected within the time span of an adiabatic compression.

The data obtained from all the tests indicate that the threshold temperatures for a fluorine/metal reaction resulting from adiabatic compression varies inversely with the final fluorine density for a given metal. However, the failure to achieve reaction under some apparently drastic conditions, indicate that some factor other than just final temperature and density has an important influence on a metal's susceptibility to reaction via adiabatic compression.

SECTION V

EFFECT OF A FLUORINE LIQUID PHASE SHOCK WAVE ON METALS

Tests were conducted at the Aerojet Liquid Rocket Company (Reference 1) to determine the effects of a shock wave promulgated through liquid fluorine (water hammer effect) on the metals listed below.

304-L Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
6061-T6 Aluminum	Nickel 200

The tests were conducted in the adiabatic compression test apparatus shown schematically in Figure 8 with 2 to 3 ml of liquid fluorine condensed in the U-tube. The configuration of the test specimen of the metal was the same as described in Section IV to facilitate discrimination between the results of adiabatic compression and the "water hammer effect." Prior to the tests with fluorine, the apparatus was checked out with water in the U-tube and with various driving pressures. The resultant pressure spikes were recorded with a 6K Tabor transducer. With a 1000 psig driving pressure, a pressure spike of 8300 psig was measured showing that the pressure in the shock wave front was approximately eight times the driving pressure. Similar results were obtained with 2000 and 3000 psig of driving pressure; however, the transducer was mechanically stopped at 9500 psig and the absolute peak pressures were beyond the range of the transducer.

The experimental data obtained with liquid fluorine are presented in Table XVII. The significant items to be noted from the data are that: (1) 304-L stainless steel and Inconel 718 were apparently not attacked during the tests; (2) Monel K-500 showed discoloration due to localized heating; and (3) 321 and A-286 stainless steels, 6061 aluminum, OFHC copper, and Nickel 200 underwent very slight attack as evidenced by the removal of the sharp edges from the test specimen. It must be emphasized that none of the attack observed in these "water hammer" tests led to significant destruction of the metal. The effects were noted by microscopic examination of samples at 40X magnification. Baseline tests, using water with 301 cryoformed stainless steel and 6061 aluminum, showed no significant attack.

The results of a related shock wave test have been reported by Douglas Aircraft Company in Reference 8. An aluminum casting alloy, A 356-T6, Grade III-F, was exposed to an explosive shock of 120,000 psi after a 24-hr soak in LF_2 (0.02% vol HF) at -320°F using a test apparatus of the card-gap type. The test resulted in a reaction with no trace of the test coupon remaining.

Generally similar tests were made by Sterner and Singleton (Reference 10) to investigate the possibility of metal ignition in liquid fluorine under conditions of explosive shock. The runs were carried out in metal tubes 2-in. long x 5/8-in. ID x .065-in. wall thickness, with the tubes themselves being the samples. The tubes were closed at the ends by brass plugs, silver soldered in place, and fluorine was added through a 1/4-in. copper tube mounted in the sample tube wall. Two tubes of each material were tested, including Monel, nickel, brass, copper, 304 SS, 316 SS, 347 SS, and 1100 aluminum. The experimental procedure was as follows:

TABLE XVII

BEHAVIOR OF VARIOUS METALS
SUBJECTED TO A SHOCK WAVE OF LIQUID FLUORINE

METAL	INITIAL LIQUID TEMPERATURE, °F	DRIVING PRESSURE, psig	RESULT
304-L Stainless Steel	-321	2000	No observable effect (2 samples)
321 Stainless Steel	-321	2000	No observable effect
321 Stainless Steel	-321	2000	Slight erosion of sample edge
A-286 Stainless Steel	-321	2000	Erosion of sample edges
A-286 Stainless Steel	-321	2000	Erosion of sample edges
6061 Aluminum	-321	2000	No observable effect
6061 Aluminum	-321	2000	Erosion of sample edges
OFHC Copper	-321	2000	No observable effect
OFHC Copper	-321	2000	Erosion of sample edge
Monel K-500	-321	2000	Discoloration due to heating
Monel K-500	-321	2000	Discoloration due to heating
Inconel 718	-321	2000	No observable effect (2 samples)
Nickel 200	-321	2000	No observable effect
Nickel 200	-321	2000	Erosion of sample edges

V, Effect of a Fluorine Liquid Phase Shock Wave of Metals (cont.)

(1) The 1/4-in. tube was attached to the fluorine gas manifold and a No. 6 electric blasting cap was tightly fastened to the tube wall with nichrome wire.

(2) An insulated can was positioned and liquid nitrogen was added to the can, covering the cell completely.

(3) Fluorine gas was condensed into the cell, filling it completely with liquid.

(4) Ten minutes after the tube was filled, the blasting cap was set off.

The ends of the tubes were usually blown out by hydrostatic pressure generated by the deformation of the tube walls, but no evidence of fluorine reaction was observed in any run.

The reactivity of titanium filings with liquid fluorine was examined by placing filings in small Monel tubes, adding liquid fluorine, and exploding a dynamite cap outside the tube. Three tests were run. In two cases, there was no apparent explosion of the titanium, although the filings were completely transformed to the white titanium tetrafluoride. In the third case, a severe detonation occurred before the cap was exploded, and the tube was torn longitudinally from the force of the blast. No trace of the filings or reaction products was found.

From the composite results of these tests, it is concluded that the shock waves generated in liquid fluorine by driving the fluorine against a dead end at a driving pressure of 2000 psig or by the close-coupled explosive shock of a No. 6 blasting cap have little or no ability to initiate a significant reaction with aluminum, brass, copper, Inconel, Monel, nickel, and austenitic stainless steels. Aluminum casting alloy A 356-T6, Grade III-F, will react with liquid fluorine under the influence of an extreme shock wave (120,000 psi). Titanium, in finely divided form, is very reactive with liquid fluorine under the influence of little or no shock wave action.

SECTION VI

EFFECT OF ULTRASONIC AND LOW FREQUENCY VIBRATION ON THE INTERACTION OF METALS WITH FLUORINE

A. ULTRASONIC VIBRATION IN THE PRESENCE OF LIQUID FLUORINE

Tests were conducted at the Aerojet Liquid Rocket Company (Reference 1) to determine whether the "passive film" on the various metals undergoes appreciable degradation when subjected to ultrasonic vibration/cavitation in the presence of liquid fluorine. The metals investigated are listed below.

301 Cryo Stainless Steel	6061-T6 Aluminum
304-L Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
347 Stainless Steel	Monel K-500
A-286 Stainless Steel	Nickel 200

The tests were conducted in the following manner. A stainless steel cylinder was fabricated with four vertical rows of welded-on B-nut cap assemblies. The metal specimens were mounted by strapping to AN plugs which sealed the B-nut cap assemblies. In this manner, eighteen metal specimens could be tested concurrently. The assembled stainless steel cylinder was immersed in an ultrasonic cleaning bath which was driven with 400 watts at a frequency of 62.5 k Hz. The specimens were passivated in fluorine vapor overnight prior to exposure to the liquid. Prior to conducting the vibration tests, a control test was made wherein the metal specimens were immersed in static liquid fluorine for 5.5 hours, then weighed to determine whether weight changes occurred. New metal specimens were installed in the test fixture. The fixture with metal specimens in place was passivated overnight and then subjected to the vibration test. The vibration test cycle consisted of one-half hour of operation, one-half hour of shutdown, and this was continued for 6 cycles. Upon completion of the vibration test cycle, the specimens were weighed.

The results of the static exposure and vibration exposure tests with liquid fluorine are presented in Table XVIII. In addition, the results of a second control test obtained with Freon-113 under the vibrating conditions are included in the table for comparison. The specimens were examined at 60X magnification to determine if significant attack had occurred. Weight changes of $\pm$ 0.1 mg are considered to be the approximate sensitivity limits of the weighing procedure.

The significant items to be noted from the data on the control tests given in Table XVIII are: (1) ultrasonic vibration of the metal specimens in the "inert," Freon 113, results in no significant weight change (average weight change is +0.036 mg, σ = 0.073 mg, and the maximum weight change lies within 2σ of the average) and only slight superficial visual effects on the surfaces, (2) static exposure of the metals, except for 347 stainless steel, to liquid fluorine results in no significant weight change (average weight change is 0.000 mg, σ = 0.056 mg, and the maximum weight change, excluding

TABLE XVIII

EFFECT OF ULTRASONIC VIBRATION ON "PASSIVE FILMS" ON VARIOUS METALS IN THE PRESENCE OF LIQUID FLUORINE

Metal	Static Exposure in Liquid Fluorine			Vibration Exposure in Liquid Fluorine			Vibration Exposure in Freon 113		
	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations
301 Cryo Stainless Steel	249.2	-0.1	No Change	253.9	0.0	No Change	-	-	-
304-L Stainless Steel	129.6	-0.1	Staining	123.8	0.0	No Change	-	-	-
304-L Stainless Steel	125.1	0.0	Staining	141.1	-0.1	No Change	-	-	-
321 Stainless Steel	139.9	0.0	No Change	133.7	0.0	No Change	-	-	-
347 Stainless Steel	141.8	+0.2	Staining	143.9	0.0	No Change	130.2	+0.1	Staining
347 Stainless Steel	152.3	+0.1	Staining	135.1	0.0	No Change	134.6	+0.1	Staining
A-286 Stainless Steel	181.9	0.0	Staining	189.0	0.0	No Change	184.0	+0.1	No Change
A-286 Stainless Steel	189.0	0.0	Staining	166.3	0.0	No Change	176.9	+0.1	No Change
6061-T6 Aluminum	47.9	0.0	No Change	48.9	0.0	No Change	44.0	-0.1	No Change
6061-T6 Aluminum	50.2	+0.1	No Change	53.2	+0.1	No Change	43.9	+0.1	No Change
OFHC Copper	143.7	0.0	Discolored	151.2	0.0	Discolored	153.1	0.0	Discolored
OFHC Copper	153.9	-0.1	Discolored	164.5	-0.1	Discolored	154.0	0.0	Discolored
Inconel 718	121.3	0.0	No Change	123.1	+0.1	Staining	137.4	0.0	No Change
Inconel 718	128.1	+0.1	No Change	126.4	-0.2	Staining	120.9	-0.1	No Change
Monel K-500	128.5	0.0	Staining	144.9	+0.1	No Change	158.5	+0.1	No Change
Monel K-500	132.6	0.0	Staining	142.3	+0.1	No Change	149.8	-0.1	No Change
Nickel 200	150.5	-0.1	No Change	147.0	-0.1	Staining	127.1	+0.1	No Change
Nickel 200	155.0	-0.1	No Change	127.8	-0.1	Staining	148.9	+0.1	No Change
Average		0.000			-0.011			+0.036	
Standard Deviation, σ		0.056			0.060			0.073	

VI, A, Ultrasonic Vibration in the Presence of Liquid Fluorine (cont.)

347 S.S., is within 2σ of the average), and (3) 347 stainless steel appears to suffer very slight attack by static fluorine as evidenced by a weight change that differs from the average of the other metals by 3.6σ. Using the above baseline statistical information, the following conclusions are reached regarding the effect of ultrasonic vibration on metals in the presence of liquid fluorine.

(1) None of the metals tested exhibit any appreciable change in weight or visual appearance other than staining or discoloration (average weight change = -0.011 mg, σ = 0.060 mg, maximum deviation = 3.2σ), and

(2) The weight change observed with Inconel 718 is very slight but may be statistically significant.

In related tests at Douglas Aircraft Company (Reference 8), the aluminum casting alloy, A 356-T6, was exposed to liquid fluorine (0.02% vol HF) at -320°F and subjected to vibration at 27.8 k Hz in an ultrasonic mechanical stepped horn apparatus in repeated cycles of 0.5 hr on and 3 hr off. Similar tests were conducted with water and liquid nitrogen for comparison. The average sample weight changes in water, LN_2, and LF_2 were 0.01, 0.02, and 0.04 mg/cm^2-min, respectively. Average corrosion pit depths in LN_2 and LF_2 were 18 and 40 microns, respectively.

It should be noted that the ultrasonic vibration involved in these tests was sufficiently powerful to disrupt the surface very significantly as evidenced by weight loss and pitting when the specimen was exposed to the inert liquid nitrogen. The fact that the presence of liquid fluorine in this same highly disruptive environment does not lead to gross fluorine/metal reaction very strongly indicates that the "passive flim" or loss of such is not an item of great importance in liquid fluorine/metal compatibility.

B. LOW FREQUENCY VIBRATION IN THE PRESENCE OF GASEOUS FLUORINE

In work reported by Sterner and Singleton (Reference 11), tubes made of copper, brass, stainless steel, nickel, and Monel which had been filled with liquid fluorine and impacted were immediately filled with gaseous fluorine after the impact test and subjected to a vibration test. The vibration test conditions were 30 Hz at 5 mm amplitude for periods up to 5 hr. In eight such tests, the vibrations produced no observable effect on the tubes. From these tests, it is concluded that low frequency vibration is insufficient to disrupt the "passive flim," or that the "passive film" is not particularly important in regard to ambient temperature gaseous fluorine/metal compatibility.

SECTION VII

RESPONSE OF METALS TO FLEXURE IN A FLUORINE ENVIRONMENT

A. ELASTIC FLEXURE IN GASEOUS AND LIQUID FLUORINE

Sterner and Singleton (Reference 11) investigated the effects of flexing thin metal strips of aluminum, brass, copper, and Monel within the elastic region in liquid fluorine using a specially designed testing cell. The tester utilized strip specimens ~3-1/2-in. long by ~3/8-in. wide by 0.001 to 0.010-in. thick. The strips had one end fixed to the bottom of the cell and the other end fastened to a reciprocating rod. This rod passed through a brass bushing in the top of the cell, and was powered by a solenoid. The solenoid was actuated by a signal from an electric timer which operated at the rate of 1 pulse/sec. The flexing tests were performed to provide information on the flexibility of a protective fluoride film. If increased corrosion resulted, this would have provided evidence that a fluoride film was present and that the film was not flexible. Evidence of corrosion was based on specimen weight change and microscopic examination at 60X magnification. The negative results actually obtained indicate that either the protective fluoride film is flexible or that a fluoride film is not required for protection. The results of these tests are summarized in Table XIX.

TABLE XIX

RESPONSE OF METALS TO ELASTIC FLEXURE IN LIQUID FLUORINE

Metal	Testing Time, min.	Flexure Cycles	Initial Specimen Wt., mg	Weight Change, mg	Observations
Aluminum (Alcoa Foil, 0.001-in. thick)	210	12600	35.8	+1.5	No change
Brass (yellow, 0.010-in. thick)	90	5400	908.4	-0.9	Sparse white coating
Copper (0.010-in. thick)	240	14400	900.3	+1.6	No change
Monel (0.002-in. thick)	290	17400	321.6	+2.0	Very sparse white splotches on convex side of sample

In related tests reported by Asunmea, et al., (Reference 12), metal specimens of 316 stainless steel and copper in the form of bellows were exposed to elastic flexure and/or cryoshock in gaseous and liquid fluorine environments to evaluate the mechanical stability of fluoride films. The basic test apparatus consisted of a double walled stainless steel test container, a specimen mount attached to the lid (to allow translational reciprocating motion of the specimens),

VII, A, Elastic Flexure in Gaseous and Liquid Fluorine (cont.)

a metal bellows seal on the reciprocating shaft, a variable eccentric cam to change the axial displacement of the shaft, and a variable speed power unit. The jacket of the test container contained no direct plumbing connections with the interior of the container and was used as a temperature control bath by flowing water or liquid nitrogen through it during different tests. A particle collector was connected at the bottom of the test chamber and was immersed in liquid nitrogen to maintain it at -320°F when necessary. The bellows specimens were formed from cold rolled, mill annealed (dead soft) sheet. The sheets were rolled into a tube, butt welded and hydroformed to contain three outside convolutions. During fabrication of the bellows, the weld was work hardened (1/8 to 1/4 full hard). During testing the axial displacement of bellows from the rest position was maintained such that the maximum stresses at the root of the convolutions was equal to 75% yield stress. This stress level is within the elastic region.

The mechanical stability of fluoride films was evaluated by low cycle fatigue tests, 5 cycles/sec, in the test apparatus according to the following four test procedures:

Test 1 - The metal bellows is exposed to gaseous fluorine at 1 atm for 1 hr, flexed for 500 cycles, and then thermally shocked and flexed in liquid nitrogen for an additional 1500 cycles. The liquid nitrogen containing any spalled-off fluoride film is drained into the cooled particle collector. The test chamber is reheated to room temperature and the low cycle fatigue and thermal shock treatment is repeated four more times. The particle collector is warmed up after the last test cycle. After the test chamber and particle collector are evacuated, the test chamber is flushed with 500 cc of filtered Freon TF which is drained into the particle collector. The contents of the particle collector are discharged through a 0.45-micron millipore filter unit. The millipore filter unit is capped-off and the 0.45-micron filter paper is subsequently removed in a dry box. The sample is subjected to metallurgical examination and analyses.

Test 2 - Test 1 procedure is repeated with the same metal bellows specimen but without flexing. The metal bellows and filter paper samples are subjected to metallurgical examination and analysis.

Tesc 3 - A new metal bellows is passivated and tested for 2000 cycles in gaseous fluorine at 2 atm. The fluorine is flushed out with gaseous nitrogen and particulate matter is flushed into the particle collector with Freon TF. The filter paper and metal bellows are subjected to metallurgical examination and analysis.

VII, A, Elastic Flexure in Gaseous and Liquid Fluorine (cont.)

Test 4 - A new metal bellows specimen is cooled to -320°F and liquid fluorine is condensed into the test chamber. The immersed bellows is flexed for 2000 cycles and the fluorine is subsequently drained into the particle collector. The test apparatus is purged free of fluorine with gaseous nitrogen and particulate is flushed into the particle collector with Freon TF. The filter paper sample and metal bellows are subjected to metallurgical examination and analysis.

A test of a 316 stainless steel bellows which involved repeated flexing in gaseous fluorine and liquid nitrogen according to the Test 1 procedure resulted in the recovery of a "structureless" material and test system contaminants. The "structureless" material was found to consist mainly of iron oxides but iron fluorides and their hydrates were identified. The same bellows was subjected to repeated gaseous fluorine and liquid nitrogen exposure without flexing according to the Test 2 procedure. This test yielded more system contaminants with adherent particulate material. The adherent material was primarily Fe_2O_3 and NiO with minor amounts of iron and nickel fluorides and iron fluoride hydrates. Examination of the bellows at approximately 30X and 100X magnification revealed only minor areas of attack on the bellows edges which were under maximum tension, and localized mechanical damage from handling.

Three different copper bellows were tested according to Test 1, Test 3, and Test 4 procedures, respectively. Analyses of recovered filter residues indicated the presence of copper, CuO, $Cu(OH)_2$, and a trace of CuF_2. Microscopic inspection failed to reveal any significant attack.

The combined data indicate that the fluoride films are stable to flexing in the elastic region of the metals in both gaseous and liquid fluorine and to cryoshock. The maximum depletion the fluoride film from the metal surface was estimated to be 0.007%.

B. PLASTIC FLEXURE IN GASEOUS AND LIQUID FLUORINE

Douglas Aircraft Company (Reference 8) conducted tests to evaluate the effects of the possible loss of the fluoride film on the surface of materials undergoing flexure/vibration in fluorine environments. The general concern was the reduction in cycle life of feed system components caused by breakdown of the passivation film.

The convoluted bellows constitute the most common form of flexible joint for state-of-the-art fluorine feed systems and was selected for testing. The test plan was designed to evaluate three potential bellows materials (Al 6061-T6, Inconel 625, and Armco 21-6-9) in gaseous and liquid fluorine and in ambient air and liquid nitrogen as control media and to test each material at three stress levels. A wide range of stress levels is used in

VII, B, Plastic Flexure in Gaseous and Liquid Fluorine (cont.)

designing conventional convoluted bellows. Commercial grade bellows are normally designed for a cycle life of 10^5 to 10^6 cycles, which result in fiber stresses that are in the elastic range for the material. Aerospace bellows, which are flight-weight feed systems, are normally designed for a cycle life of 10^3 to 10^4 cycles and, therefore, the fiber stress may be in either the elastic or in the plastic range of the material. Stress loadings that loaded the test specimens into the plastic range were selected for these tests. This decision was based on the three following factors: (1) aerospace bellows may be loaded in the plastic range, (2) adverse effects from exposure to fluorine would normally be more pronounced when the specimen is stressed in the plastic range, and (3) test time would be minimized.

The apparatus used for bellows testing consisted primarily of a specimen actuation shaft, which was actuated by an eccentric cam driven by a variable-speed electric motor. The complete drive mechanism was mounted on an unjacketed lid assembly. The original testing concept involving the use of the bellows specimens as the return mechanism for the eccentric drive became invalid when specimen loadings into the plastic range were selected for evaluation. Auxiliary return springs were added to the drive assembly to ensure proper return motion. With the addition of the return springs it was not possible to determine failure of a single test specimen by the loss of proper cam follower return action. Therefore, it became necessary to incorporate a different test technique to determine the first specimen failure. This alternate method consisted of operating the test assembly for a fixed number of cycles and then stopping the device, while the specimens were examined. This method resulted in test data points that had some scatter because the exact cycle of failure was not detectable.

Testing was conducted in four media: (1) ordinary air at ambient temperature and pressure; (2) liquid nitrogen at atmospheric pressure and its normal boiling point (-320°F); (3) gaseous fluorine at ambient temperature and 0.5 psig pressure; and (4) liquid fluorine at -320°F, pressurized with helium to 0.5 psig. The data show a consistent reduction in cycle life during the fluorine tests of approximately 30% as compared to the control runs. This percentage holds true for both ambient and cryogenic testing. The exact cause of the cycle life reductions was not determined.

The results of the flexure tests on 6061-T6 aluminum, Armco 21-6-9, and Inconel 625 bellows specimens in each of the test environments (ambient air, gaseous fluorine, liquid nitrogen, and liquid fluorine) are summarized in Table XX. These data, after appropriate analyses and reduction, have been correlated to yield fatigue strength-endurance cycle curves for each material in each environment. These correlations are presented in Figures 9, 10, and 11 for 6061-T6 aluminum, Armco 21-6-9, and Inconel 625, respectively.

TABLE XX

FATIGUE LIFE OF FLEXED METAL BELLOWS IN GASEOUS AND LIQUID FLUORINE

Bellow Material	Nominal Root Stress Level, psi x 10^{-3}	Ambient Air		Gaseous Fluorine		Liquid Nitrogen		Liquid Fluorine	
		Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}
6061-T6 Aluminum	69.9	9/9	4*	1/2	3.5-3.0	4/4	35-40	2/2	<25
	90.0	4/4	2.0-2.5	1/2	1.0-1.5	--	--	2/2	<15
Armco 21-6-9	99.5	2/2	40-60	2/2	<20	--	--	--	--
	125.0	2/2	>10	--	--	1/1	>100	--	--
	175.0	2/2	10-20	2/2	12-17	2/2	<48	1/2	<21
	202.0	--	--	--	--	1/2	50-60	1/2	>48
	268.0	--	--	1/2	2.0-4.0	2/2	20-30	--	--
Inconel 625	91.0	1/2	6-20	--	--	--	--	2/2	25-30
		1/2	>80					--	--
	147.0	1/1	>10	--	--	1/4	45-50	--	--
	200.0	1/2	10-20	1/2	12-15	3/4	>100		
						2/2	<48	1/2	<21
	290.0	--	--	--	--	1/2	15-20	1/2	>48
	294.0	2/4	<10	--	--	1/2	20-30	--	--
	396.0	--	--	2/2	2-4	--	--	--	--
						2/2	7-10	2/2	8-12

* Mean value

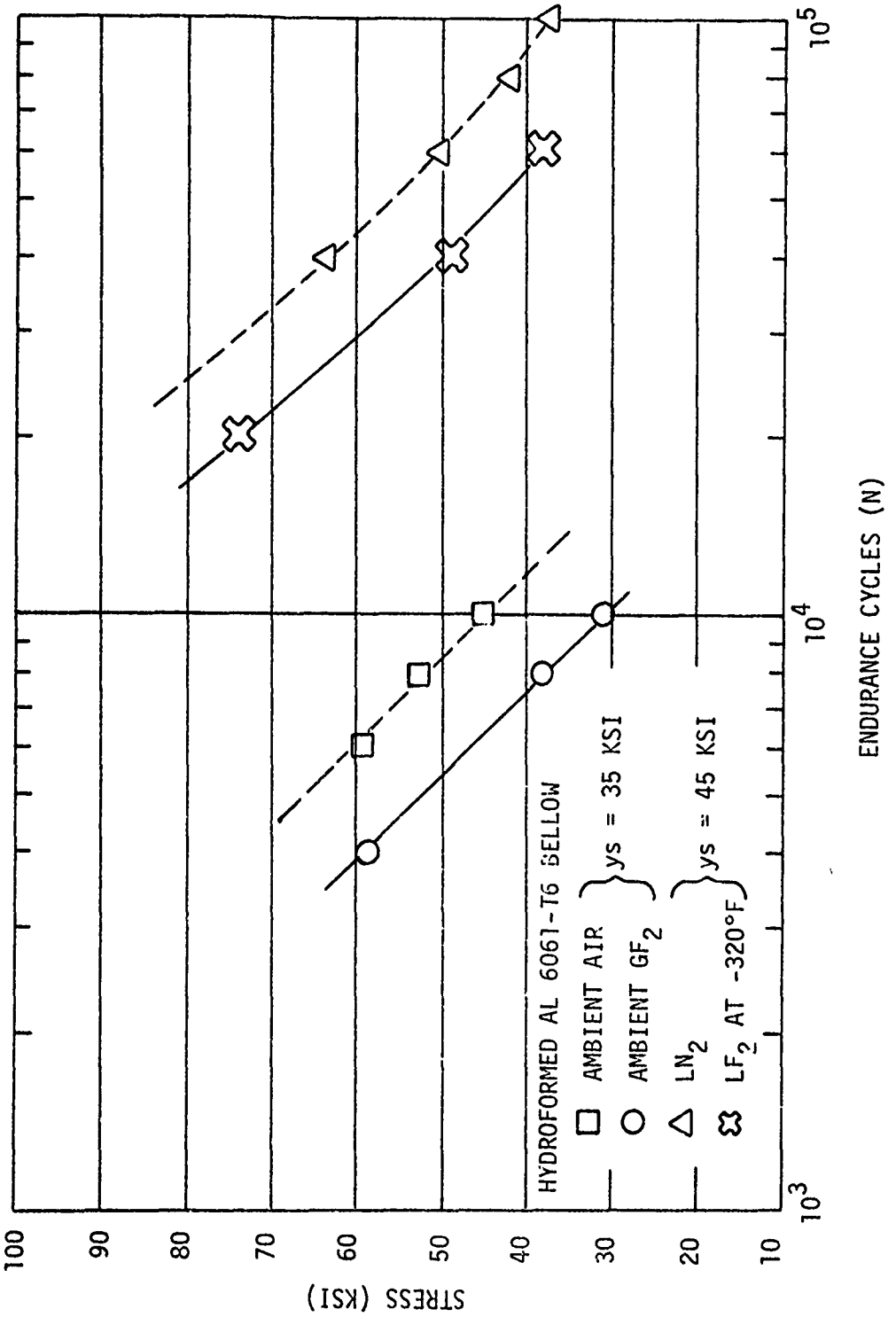

Figure 9. Fatigue Strength of Hydroformed 6061-T6 Aluminum Bellows in Fluorine Environments

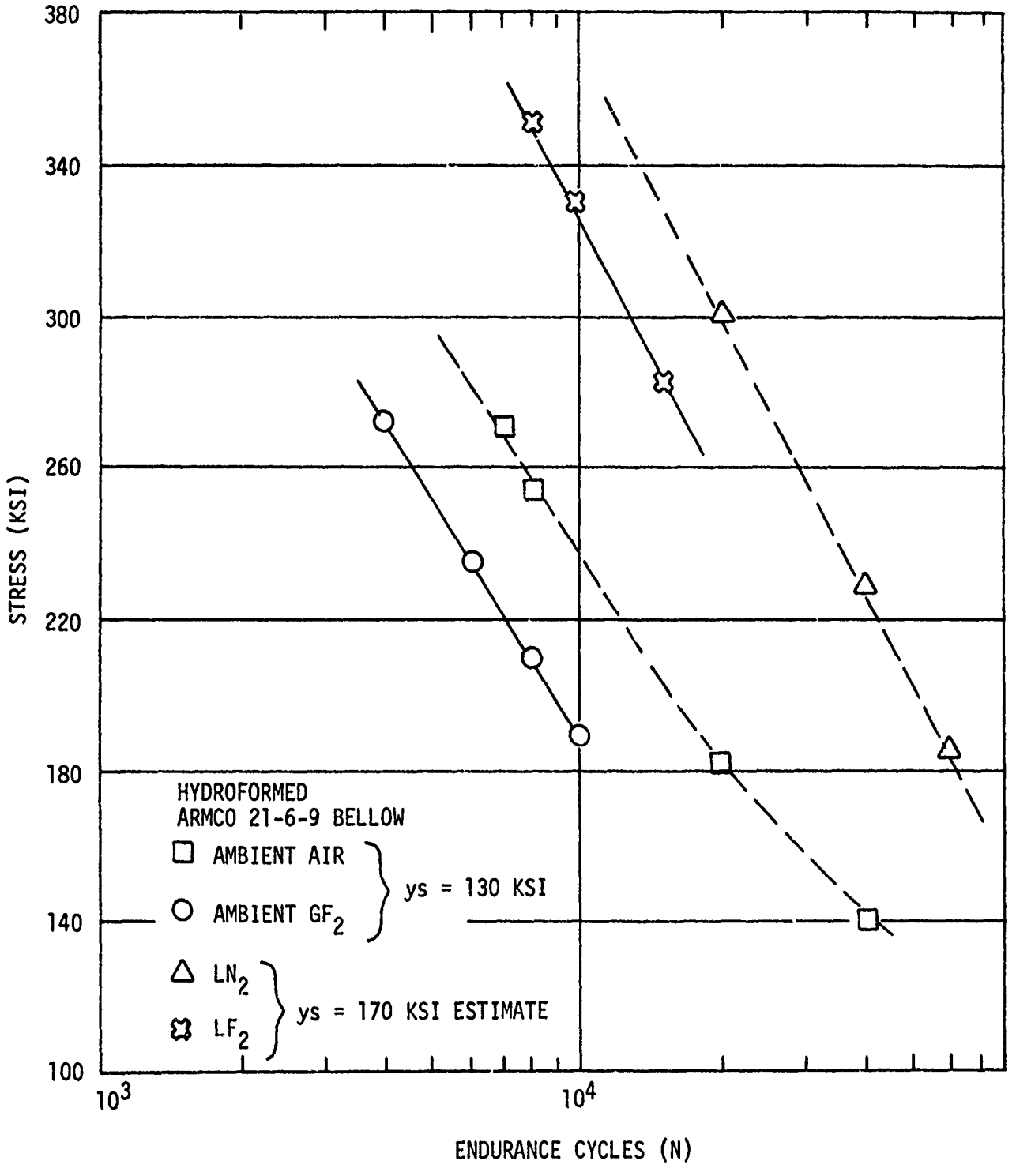

Figure 10. Fatigue Strength of Hydroformed Armco 21-6-9 Bellows in Fluorine Environments

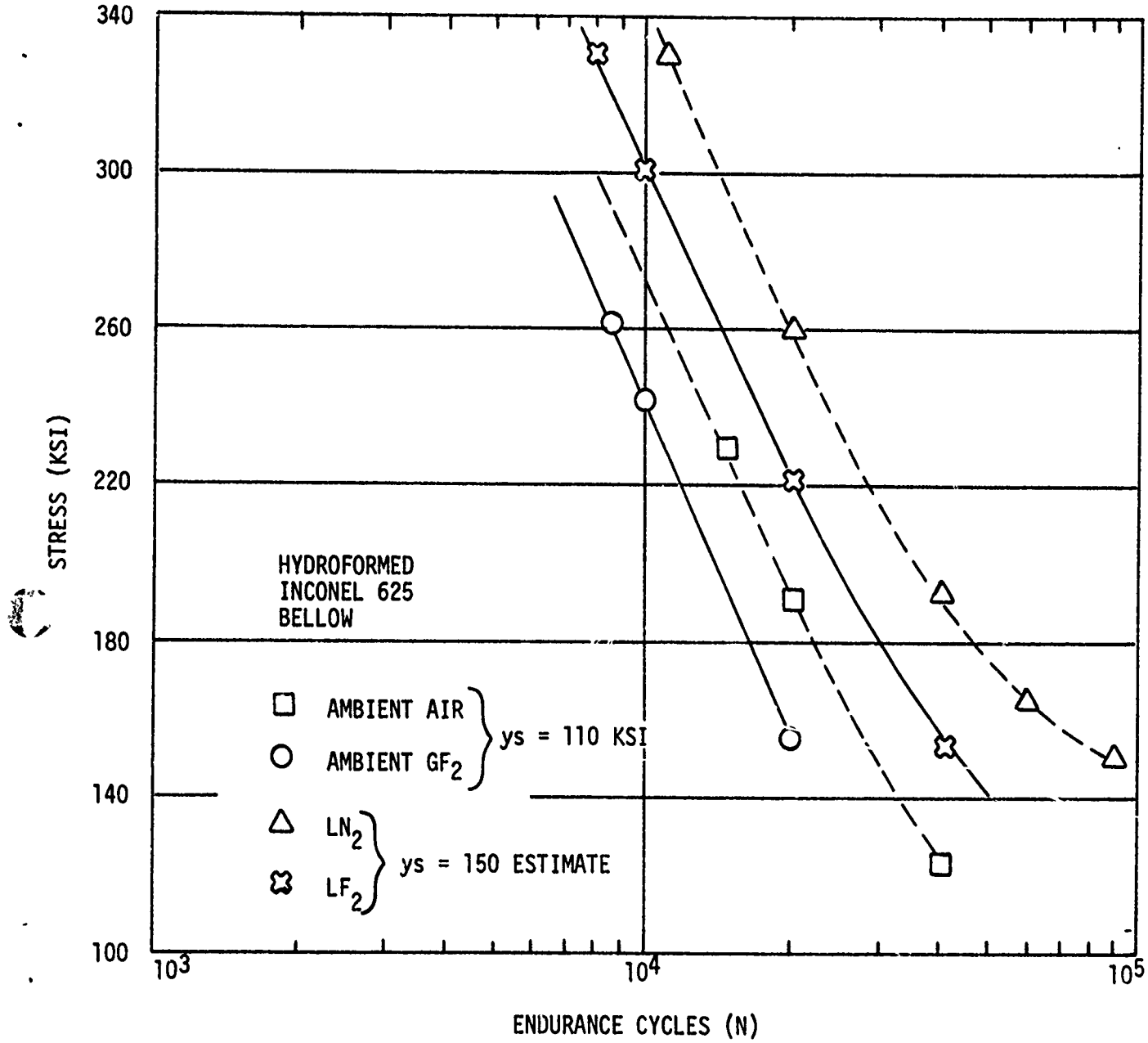

Figure 11. Fatigue Strength of Hydroformed Inconel 625 Bellows in Fluorine Environments

SECTION VIII

EFFECT OF MECHANICAL IMPACT ON METALS IN THE PRESENCE OF FLUORINE

Apparently, Sterner and Singleton (Reference 11) were the first to investigate the effect of mechanical impact on metals in the presence of fluorine. The metals they studied are listed below:

304 Stainless Steel	Brass
316 Stainless Steel	Copper
321 Stainless Steel	Monel
347 Stainless Steel	Nickel

The metal specimens were in the form of tubes cut to 2-in. lengths. Brass plugs were made up to fit the bore of each tube and they were silver soldered into the ends of the tube. A 1/4-in. copper tube was silver soldered into a hole drilled into the side of the tube. Tubes were cleaned after this with dilute hydrochloric acid, neutralized, rinsed and thoroughly dried. The tube was supported in a test cabinet in a horizontal position by a suitable mounting and a sharp conical stainless striker was positioned on the upper surface of the tube. The tube was evacuated, immersed in liquid nitrogen, and completely filled with liquid fluorine. Impact was provided by dropping either a 4- or a 6-lb weight onto the striker. Impact energies of approximately 1 to 10 ft-lb were used, depending on the thickness of the tube wall. In most cases, the impact was just below that necessary to rupture the tube wall, while in a few cases the wall was actually ruptured.

These tube impact tests were intended to test the hypothesis that a fluoride film protects the metal surface at low temperatures. It was reasoned that a severe blow on the tube wall would stretch the metal sufficiently to break the film and expose bare metal to the liquid fluorine. In many cases, the impact was severe enough to produce cracks on the inside wall of the tube and in 5 cases out of 20, the tube was ruptured. No ignition or increased corrosion was apparent or detected upon examining the impacted area microscopically with any of these metals.

At about this same time period it became known that titanium may ignite in liquid oxygen under the stimulus of a suitable mechanical impact (Reference 13). On the basis of that evidence, it was suspected that titanium and possibly some of the other metals would be sensitive to impact with liquid fluorine. Sterner and Singleton (References 10 and 11), therefore, performed tests to establish the energy level required to ignite titanium in liquid fluorine. In general, the tests were accomplished by dropping weights of various sizes from various heights or by releasing a compressed spring to obtain suitable impact energies. These energies ranged from 2.6 to 65 ft-lb. The samples and strikers were examined microscopically for evidence of ignition and the results were reported in a qualitative manner. The samples were polished 1/2-or 5/8-in. squares of metal and 0.050-in. thick. The sample and all of the components of the impact cell were scrupulously cleaned and dried before being placed into

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

the cell. Several striker materials and a variety of striker faces were used in the tests. The preliminary work was performed using Monel strikers with titanium samples. Later work used titanium strikers with titanium samples. A few tests were conducted with aluminum and stainless steel strikers on aluminum samples. The types of strikers which were used are as follows:

Flat smooth	-	polished circular striking face, 1/8 to 3/8-in. diameter;
Flat rough	-	3/8-in. dia. circular striking face scarred with file marks;
Flat grooved	-	1/4-in. dia. circular striking face grooved similarly to phonograph record;
Chisel pointed	-	striking face was 1/4-in. knife edge;
Conical pointed	-	sharply pointed with 60° included angle;
Hollow pointed	-	small flat tip with 1/6-in. hole drilled into it;
Round	-	hemispherical striking face, 1/8 in. radius.

The results of these impact tests are summarized in Table XXI. The impact levels listed were calculated from the weight and distance dropped for the dropweight tests, and in the case of the spring-driven plunger, the energy level was calibrated by cocking the spring against a calibrated spring-scale. Ignition, when it was observed, was indicated by the formation of small craters and gullies together with droplets of melted metal on the sample or on the striker face. Usually the crater or gully formation on the sample was mirrored almost exactly on the face of the striker. The direction of ignition was generally away from the center of impact.

The preliminary tests with Monel metal strikers and titanium samples provided the surprising result that the striker tip reacted with the fluorine even at very low impact levels, but the sample did not. This indicated that the configuration of the striker face played as large a part in inducing ignition as did the impact energy level. This impression was strengthened in later tests as higher impact levels were used.

Various strikers were used in the hope of obtaining reasonably reproducible ignitions. The flat, smooth strikers were intended to provide a standard for comparison. The conical and chisel point strikers were intended to deliver all of the impact energy at one spot. The hollow, pointed and flat,

TABLE XXI

EARLY IMPACT TEST RESULTS ON ALUMINUM AND TITANIUM ALLOYS IN LIQUID FLUORINE AT -320°F

Striker Material	Striker Configuration	Impact Energy, ft-lb	Calc. Max. Energy Flux, ft-lb/in.^{2}-sec	Number of Tests: Positive Reaction	Number of Tests: No Reaction
	Titanium Samples (A 110 AT and C 120 AT)				
Monel	Flat, smooth	2.6	--	0	5
	Flat, rough	2.6	--	1	1
	Hemispherical	2.6	--	1	1
	Chisel-pointed	2.6	--	2	0
	Conical, pointed	2.6	--	3	0
				7	7
Titanium	Flat, smooth	40	--	2	0
		45	1.61×10^7	3	13
		52	1.86×10^7	5	11
		55	--	2	0
		58	--	1	3
		60	2.15×10^7	10	6
	Flat, grooved	5	--	2	0
		15	--	2	0
		30	--	2	0
		55	--	1	1
		58	--	2	0
		60	--	10	2
	Conical, pointed	2.6	--	1	2
		6	--	3	0
		9	--	2	0
		35	--	1	0
		50	--	2	0
		55	--	2	0
		58	--	1	1
		60	--	8	6
		61	--	0	1
	Hollow, pointed	6	--	1	3
		10	--	2	2
		38	--	1	0
	Aluminum Samples (Al 6061)				
Stainless Steel	Flat, grooved	58	--	1	11
	Conical, pointed	58	--	0	2
Aluminum	Conical, pointed	30	--	0	10

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

grooved strikers were intended to trap some of the liquid and vaporized fluorine under the striker to provide high temperature by adiabatic compression. One problem with the conical pointed strikers at the higher energy levels was the welding of the tip to the sample surface. This made it difficult to detect whether ignition had occurred.

As can be seen in Table XXI, the results were not very reproducible and in no case did ignition become general. There was no apparent difference between the two titanium alloys tested. With aluminum, one ignition was obtained out of 24 tests. With titanium, ignition was initiated by all types of strikers at different impact levels. The effectiveness of ignition by the various striker configurations in increasing order was: flat; smooth; pointed; and grooved.

The next definitive work was reported by Douglas Aircraft Company (Reference 8) in 1967, by which time a modified ABMA impact test apparatus had become a relatively standard means of determining the impact sensitivity of materials in cryogenic oxidizers (particularly liquid oxygen). They performed open cup impact tests with liquid fluorine at -320°F and aluminum-silicon casting alloy, A356, (Types IV, III, II, and I, in order of increasing quality) using a modified ABMA impact test apparatus at an impact energy of 72 ft-lb*. Many of the test samples cracked upon testing (the frequency of cracking decreasing as the quality of the alloy increased) but even with the formation of new metal surfaces from sample cracking, reactions were not initiated. Samples which had previously been dye-penetrant inspected using both organic and inorganic dye penetrants and then thoroughly cleaned and baked in a vacuum prior to impact testing showed that the penetrants lead to increased impact sensitivity and, thus, are not safe quality inspection tests of cast materials for fluorine service. A closed-cup impact test at the 72 ft-lb impact level on aluminum A 356-T6, Grade III-F, which had been immersed in liquid fluorine at -320°F for 21 days showed no sign of reaction initiation but cracked similar to specimens used in open-cup tests. These tests showed quite conclusively that aluminum has a low level of sensitivity to impact in liquid fluorine but contaminants such as dye penetrants can increase the impact sensitivity.

Toy, et al., (Reference 14) have reported the results of three series of impact tests on 2014-T6 aluminum and Ti-6Al-4V(ELI) titanium in liquid fluorine. These tests are described in the following three paragraphs and the test results are summarized in Table XXII.

* Materials that are not initiated in liquid oxygen by an impact of 70 or 72 ft-lb on a modified ABMA impact tester are generally considered sufficiently impact insensitive to be considered for liquid oxygen service.

TABLE XXII

IMPACT TEST RESULTS ON 2014-T6 ALUMINUM AND Ti-6Al-4V(ELI) TITANIUM IN LIQUID FLUORINE

Metal Specimen	Striker Material	Sample Cup Material	Liquid Fluorine Temp., °F	Impact Energy, ft-lb	Number of Tests: Positive Reaction	Number of Tests: No Reaction
Al 2014-T6	17-4 PH	Al 1100	-320	70	0	20
Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	-320	≤43	0	2
				47	1	7
				47.5	0	1
				48	1	1
				48.5	1	0
				49	1	0
				50	0	1
				≥51.5	2	0
Ti-6Al-4V	Ti-6Al-4V	Al 1100	-320	47	0	1
				58.5	1*	0
				70	1	0
Ti-6Al-4V	17-4 PH	Ti-6Al-4V	-320	≤72	0	5
Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	-240±10	≥40	3	0

* Reaction on rebound only

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

Modified ABMA open cup impact tests were conducted on specimens of 2014-T6 aluminum at an impact energy of 70 ft-lb in liquid fluorine (-320°F) using 17-4 PH stainless steel strikers and Al 1100 sample cups. No reactions were observed in 20 tests.

Modified ABMA open cup impact tests on Ti-6Al-4V(ELI) titanium in liquid fluorine indicated it was impact sensitive when the following test combinations were used: (1) Ti-6Al-4V(ELI) sample, striker, and cup; and (2) Ti-6Al-4V(ELI) sample and striker and Al 1100 cup. The energy for a 50% probability of initiating a reaction with test combination (1) in liquid fluorine at -320°F was calculated to be 48 ft-lb. The test combination (2) was found impact sensitive at 70 ft-lb. The test combination Ti-6Al-4V(ELI) sample and cup and 17-4 PH striker pin was not impact sensitive in liquid fluorine at 72 ft-lb.

Three drop-weight closed cup impact tests were conducted with liquid fluorine at -240 $\pm$ 10°F (485 $\pm$ 15 psig) in the following manner: 86 cc of gaseous fluorine was condensed in the test unit at -320°F; the test assembly was allowed to warm up by letting the liquid nitrogen evaporate from the cryogenic bath; temperature and pressure were recorded and the drop-weight released when the pressure reached 500 psig. In these reactive impact tests, a 10 to 30 psi pressure drop in the test bomb was observed when impact occurred. Examination of the Ti-6Al-4V(ELI), sample, striker, and cup revealed numerous reaction sites. This impact energy value was deliverately chosen to be less than the open cup E_{50} of 48 ft-lb required for a 50% probability of initiating a reaction at -320°F in liquid fluorine. Qualitatively, the reaction found at 40 ft-lb impact energy level indicates that the titanium alloy is more impact sensitive in liquid fluorine at -240°F than at -320°F. This is borne out by the numerous reaction sites observed on the sample, striker, and cup.

Endicott and Donahue (Reference 15) have performed open cup impact tests with liquid fluorine (-320°F) and gaseous fluorine (65°F, ambient pressure) and titanium alloy, Ti-5Al-2.5Sn (ELI), with a modified ABMA impact test apparatus at an impact energy of 72 ft-lb. With liquid fluorine two reactions were observed in two tests and with gaseous fluorine no reactions were observed in 20 tests.

From all of the mechanical impact tests performed on metals in a liquid fluorine environment, it is concluded that the titanium alloys are the only ones among those studied that exhibit a significant sensitivity to impact at or below the 72 ft-lb energy level on a modified ABMA impact tester. The sensitivity of titanium to impact in the presence of liquid fluorine at -240°F appears to be greater than at -320°F but the sensitivity to gaseous fluorine at ambient temperature and pressure is less than for the liquid phase at -240 or -320°F. Aluminum alloys do not appear impact sensitive in the presence of liquid fluorine at -320°F and an energy level of 70-72 ft-lb (ABMA impact tester) unless the specimens are contaminated.

SECTION IX

RESPONSE OF METALS TO FRICTION, ABRASION, AND FRACTURE IN A FLUORINE ENVIRONMENT

A. METAL/METAL FRICTION IN GASEOUS FLUORINE

Theoretical analyses reported by Endicott and Donahue (Reference 15) indicate that a coefficient of friction of 0.40 would be expected for dissimilar metals operating in air and a value of 0.10 to 0.18 with a fairly good lubricant. To evaluate the silver-stainless steel combination in a gaseous fluorine environment, tests were conducted using a frictional-energy test device. To conduct this test, a frictional-energy test disk was refinished and given a silver plate. During the refinishing, a series of ventilation slots were cut into the test specimen so that gaseous fluorine exposure of the contact surfaces could be assured. After installation of the test specimen in the apparatus, the test section was pressurized with ambient gaseous fluorine and a series of friction runs was conducted up to the capacity of the machine. The results of the tests are shown on Table XXIII. During the last two tests, the samples were loaded so that the mechanism could not complete enough travel for a realistic value of friction coefficient to be determined. Post-test inspection of the test sample showed no evidence of galling on the specimen after all five tests. The silver fluoride film was a yellow-green fine-grained coating which transferred from the silver to the 316 stainless steel in small quantities. This was judged to be an acceptable condition for dry film lubrication. The measured coefficients of friction of 0.08 to 0.20 indicate that the fluoride film provides a reasonable measure of lubrication.

TABLE XXIII

RESULTS OF FRICTION TESTS OF SILVER-316 STAINLESS STEEL IN GASEOUS FLUORINE

Test No.	Load, psi	Coefficient of Friction
1	1,000	0.20
2	1,180	0.17
3	1,980	0.08
4	4,000	--
5	6,050	--

B. METAL ABRASION IN LIQUID FLUORINE

Film disruption studies were made by Sterner and Singleton (Reference 10) in which metal surfaces were continually wire brushed while immersed in liquid fluorine. The tests were carried out in a Monel cell 1-1/4-in. ID x 4-in. deep. A wire brush 1/2-in. x 1/2-in. was made with fine

IX, B, Metal Abrasion in Liquid Fluorine (cont.)

stainless steel bristles about 1/4-in. long and attached to a 1/4-in. Monel rod which passed through a brass bushing in the top of the cell. The metal sample, about 2-in. x 3/4-in. was supported in the bottom of the cell at an angle of about 30° with the vertical. The brush was caused to move up and down on the sample by a solenoid outside the cell. The rate was 1 stroke/sec and the travel was about 1-in. The Monel rod was hinged in the middle so that the brush was free to travel along the surface of the sample, and the force exerted by the brush on the sample was constant over the whole stroke. This normal force was due largely to gravity, and was about 0.05 lb. A helium purge was maintained on this cell during operation to prevent air from diffusing into the cell through the brass bushing. Ten tests were made with copper and two with magnesium alloy AZ-31. In addition, three blank tests were made with copper and one with magnesium. These control samples were exposed to liquid fluorine in exactly the same manner as the other samples except that the brush was not attached to the rod. The results of all the tests are presented in Table XXIV.

While the weight gains on these abrasion tests are scattered from 0 to 10 mg, the average for the copper and the magnesium samples is about the same as the weight changes observed on the blanks. Because the cell was not air tight, it is quite likely that small quantities of air with its accompanying moisture were able to diffuse into the cell and cause corrosion at a slightly higher level than is commonly observed in continuous immersion tests. The abrasion was severe enough to disrupt any protective fluoride film on the metals. The fact that no increase in corrosion was observed indicates that film protection is not the controlling mechanism in the corrosion resistance of these metals to liquid fluorine.

C. METAL FRACTURE IN FLUORINE

Tensile tear tests of metals immersed in liquid fluorine were conducted by Sterner and Singleton (Reference 11) with titanium, brass, copper, Monel, and aluminum. The titanium samples were 1/4-in. diameter rods which were machined in the center to about 0.030-in. diameter. The rod was threaded on both ends with one end screwed into a socket at the bottom of the test cell. The other end was fastened to a Monel metal rod which in turn protruded through a bushing in the top of the cell. A helium purge was used to reduce atmospheric contamination. A hand-operated lever fastened to the Monel rod was used to tear the sample after fluorine had been liquefied into the cell. The other four metals were tested in the same equipment, but the samples were in the form of thin strips 3-in. x 1/4-in. x 0.005-in. The torn edges of the samples were examined microscopically at 60X.

These tests were intended to present a freshly fractured surface to the liquid fluorine environment. Thus, there could be no possibility of a fluoride film protecting the surface at the time of fracture. It was expected that resulting ignition or corrosion products would indicate the need of a film

TABLE XXIV

RESULTS OF ABRASION TESTS OF METALS IN LIQUID FLUORINE

Sample	Alloy	Initial Weight, gm	Weight Change, mg	Exposure Time, hr	Remarks
1	Copper	28.2264	0.1	1	All samples, except where
3	Copper	14.3360	0.9	1	otherwise designated, were
6	Copper	20.7717	5.2	1	brushed with a coarse stain-
8	Copper	22.3695	9.9	1	less steel brush continuously
9	Copper	20.7949	3.8	1	at one stroke/second while
10	Copper	21.8593	4.3	1	under liquid fluorine.
13	Copper	21.5263	-0.3	1	
14	Copper	22.2546	4.1	1	
15	Copper	22.2243	8.4	1	
16	Copper	22.1763	5.0	1	
		Avg.	4.14 (σ = 2.42)		
21	Copper	15.3295	3.9	1	*
22	Copper	20.8356	8.0	1	*
23	Copper	20.6760	1.0	1	*
		Avg.	4.3 (σ = 2.47)		
11	Mg AZ-31	5.8931	1.5	1	
17	Mg AZ-31	9.1126	2.9	1	
		Avg.	2.2		
20	Mg AZ-31	6.1560	2.0	1	*

* These samples were tested in the abrasion apparatus without brushing.

IX, C, Metal Fracture in Fluorine (cont.)

for protection. One barely observable ignition was obtained in six tests with titanium and this would tend to support the protective film theory. However, the ignition can also be explained by a process which involves the strain-heating of the specimen to its ignition temperature. No apparent reaction occurred when thin metal strips of copper, brass, Monel or aluminum were torn in tension under liquid fluorine.

Somewhat related test results have been reported by Richards and Hanson (Reference 16) wherein specimens of ASM 6434 steel; AM 350, 301, and 304-L stainless steel; 2014-T6, 6061-T6, and 7075-T6 aluminum, and Ti-6Al-4V titanium were fractured in liquid fluorine at -320°F in the course of tensile testing. There was no evidence of ignition on any of the specimens. Specimens of AM 350 stainless steel and Ti-6Al-4V titanium were similarly fractured in a high-velocity jet of gaseous fluorine at approximately 75°F. No indications of metal reaction were observed.

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